ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

INVESTIGATION OF THE EFFECTS OF NUCLEATING AGENTS ON THE MECHANICAL BEHAVIOUR OF RECYCLED POLYPROPYLENE

M.Sc. THESIS

Buket ŞENTÜRK

Department of Polymer Science and Technology

Polymer Science and Technology Programme

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MAY 2014

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ÇEKİRDEKLENDİRİCİ KATKILARIN GERİ DÖNÜŞTÜRÜLMÜŞ POLİPROPİLENİN MEKANİK DAVRANIŞINA ETKİSİNİN ARAŞTIRILMASI

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MAYIS 2014

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Date of Submission : 02 May 2014
Date of Defense : 27 May 2014

FOREWORD

I would like to thank my supervisor, Prof. Dr. Nurseli UYANIK whose patience and encouragement helped me during my research. I also thank for her valuable suggestions during writing of this thesis.

I sincerely thank to my co-supervisor Dr. Tolga GÖKKURT, for his invaluable help and support. His high standards for scientific investigation, guidance and encouragement have helped to complete this dissertation. It was a great honor and pleasure to work with him and benefit from his experince.

I would like to thanks to Polipro Plastic providing me opportunities to make my experimental studies.

I also would like to express my thanks to Assoc. Prof. Dr. Güralp ÖZKOÇ from Kocaeli University, Department of Chemical Engineering, for providing me an opportunity to make my some experimental studies at Kocaeli University, Polymer Laboratory.

I would like to thank Assoc. Prof. Dr. Ali DURMUŞ from Istanbul University, Department of Chemical Engineering, providing me to their laboratory facilities.

I especially would like to thank my family, Aynur ŞENTÜRK, Okhan ŞENTÜRK, Burçin ŞENTÜRK BAL, Oğuzhan TURAN, Özgür BAL for all their emotional assists and motivation during this extremely difficult accomplishment and supporting me all my life.

May 2014

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ABBREVIATIONS

PP	**:** Polypropylene
RPP	**:** Recycled Polypropylene
EPDM	**:** Ethylene-propylene-diene-monomer
NA	**:** Nucleating Agent
AO	**:** Antioxidant
ISO	**:** International Organization for Standardization
L/D	**:** Length/Diameter
MPa	**:** Mega Pascal
XRD	**:** X-ray Diffraction
DSC	**:** Differential Scanning Calorimeter
MFI	**:** Melt Flow Index
POM	**:** Polarizing Microscope

LIST OF SYMBOLS

T_c	: Crystallization temperature
T_m	: Melting temperature
ΔH_c	: Crystallization entalphy
ΔH_m	: Entalphy of fusion
α	: Alpha
β	: Beta
E_{izod}	: Izod impact strength

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INVESTIGATION OF THE EFFECTS OF NUCLEATING AGENTS ON THE MECHANICAL BEHAVIOUR OF RECYCLED POLYPROPYLENE

SUMMARY

Plastics are very important material group which has become an indispensable part of our lives because of their superior features and low prices. However, their chemical structures high resistant to hydrolytic and biological effects are the source of negativeness which allows to remain intact for a long time when abandoned to nature as waste. Today, this situation has become a major problem in terms of environmental pollution when it is combined with the “use-throw” property and the lack of recycling/recovery processes of plastics. In this regard; the accumulation of large amounts of plastic waste with annual 150 million tons of plastic consumption that said, this increased production and waste values every day in today's conditions; it is clear that plastic will bring negative effects to human health and the environment will continue to increase. The most efective and plausible solution in order to eliminate this major problem is recyling of plastics.

Polypropylene (PP) is one type of plastics having the highest consumption rate have properties such as excellent chemical and moisture resistance, high mechanical properties, low density and good processability. However, the potential of PP to be an engineering plastic has been seriously limited by its low impact strength. This situation is bigger problem for especially recycled PP raw materials. Thermal and oxidative degradation occuring in its structure before recycling process, and exposing to temperature and shear stresses causes much higher losses in terms of mechanical properties. This situation causes to brittleness of the material, deterioration of the mechanical and surface properties; also decreasing of stability and limiting the end production applications.

In this study, functional addtives were used in order to increase strength of recycled PP, extend the range applications and especially usage in sectors such as automotive industry where the impact strength has big importance. For this purpose, diaper and packing post-production wastes granulated by using plastic recycler single screw extruder were used.

Firstly, elastomeric additive used in order to increase impact strength of recycled PP. However, elastomer toughening sacrifices the mechanical properties such as tensile strength, elastic modulus and hardness. Nucleating agents (NAs) were used to overcome this drawbacks caused by using elastomeric additive. Changing of crytallization behaviour of PP was aimed with α-NAs. Besides, a synergic effect was observed by using secondary antioxidant as processing stabilizer.

In the study, recycled PP (RPP) raw material, ethylene-propylene-diene-monomer (EPDM) with 5% and 10% ratio, 3 different grades of α-NA with 0.5% ratio and secondary antioxidant with 0.2% ratio were melt-mixed. Mono, binary and ternary mixtures were prepared in order to observe effects of elastomeric additive, nucleating agents and antioxidant on recycled PP by using twin screw extruder. In addition, 3 phr black masterbatch was added in order to obtain better appearance of samples during the preparation of every mixtures. 24 samples were prepared with this method and then the prepared granulates were molded to obtain standard test samples (MFI, tensile, impact and hardness test bars and plates) by using injection molding method. Physical, morphological, thermal and mechanical properties of the effects of the additives on PP were evaluated with these test samples. Density, melt flow index (MFI), X-ray diffraction (XRD) and differantial scanning calorimetry (DSC), polarizing microscope (POM) tests were conducted to determine the structural, morphological and thermal properties of the test samples. Tensile, impact and hardness tests were also carried out to evaluate the mechanical properties of the samples.

According to density measurement results of 24 test samples, it was observed that there was not any difference between the mixtures that contains EPDM, nucleating agent and antioxidant. Granules of the samples were molten at the temperature of 230°C and a load of 2.16 kg was applied on them. It was observed that melt flow index of the materials was decreased with increasing loading level of EPDM. On the other hand nucleating agent and antioxidant did not affect to melt flow index values appreciably. According to XRD results, the effect of nucleating agent on crystallzation behaviour was determined. By using α-NA additives it was obtained that θ angle and intensity values as indicator of monoclinic structure.
In the DSC analysis; samples were heated and cooled with between room temperature and 300ºC at 10ºC/min rate. From DSC results; it is observed that nucleating agents increased crystallization temperature according to recycled PP.
Crystallization behaviour of the samples was examined with polarizing microscope (POM) attached hot-stage taking melting and crystallization temperature values determined according to DSC results as reference.
Spherulite growth kinetic of the materials was observed as well as crystallization behaivour by using polarizing microscope attached hot-stage with on-line recording. During POM analysis between 250 °C and 110 °C with 1 °C/min cooling rate; the crystallization behaviours of recycled PP, elastomeric additive and nucleating agent added mono and ternary mixtures were investigated. It was observed that nucleating agents raised the crystallization temperature and made smaller the sizes of spherulites.

According to tensile test results; tensile strength and elastic modulus of the samples decreased with addition of merely EPDM, percent strain increased. Besides, it was observed that nucleating agents and antioxidant slightly increased the tensile strength and elastic modulus, then percent strain decreased. Although EPDM, nucleating agents and antioxidant continued their effects in binary mixtures; the drawbacks

caused by EPDM addition could not be prevented. However, a synergic effect was obtained in ternary mixtures and expected results was observed in terms of tensile strength, elastic modulus, percent strain values.

According to the notched Izod impact test results, EPDM addition increased impact strength of the samples. Nucleating agent and antioxidant decreased the positive effect of EPDM on the impact strength of samples containing binary mixtures. However, in ternary mixtures impact strength dramatically increased and a synergic effect was obtained.

According to Shore-D hardness test results; EPDM decreased hardness of the samples, in contrast with the nucleating agents and antioxidant effects.

ÇEKİRDEKLENDİRİCİ KATKILARIN GERİ DÖNÜŞTÜRÜLMÜŞ POLİPROPİLENİN MEKANİK DAVRANIŞINA ETKİSİNİN ARAŞTIRILMASI

ÖZET

Plastikler; üstün özellikleri ve düşük fiyatları nedeniyle hayatımızın vazgeçilmez bir parçası haline gelmiş, çok önemli bir malzeme grubudur. Bununla birlikte, plastiklerin hidrolitik ve biyolojik etkilere yüksek dirençli kimyasal yapıları, atık olarak doğaya terk edildiklerinde, uzun süre yapısal olarak bozulmadan kalabilmelerine olanak sağlayan bir olumsuzluğun da kaynağıdır. Günümüzde, bu durum; plastiklerin "kullan-at" özelliği ve geri dönüşüm/kazanım süreçlerinin yetersizliği ile birleştiğinde, çevre kirliliği açısından büyük bir sorun haline gelmiştir. Bu bağlamda; yıllık 150 milyon tonluk bir plastik tüketimi ile birlikte yüksek oranlarda plastik atık birikiminin söz konusu olduğu, bu üretim ve atık değerlerinin her geçen gün arttığı günümüz koşullarında; plastiklerin çevre ve insan sağlığına getireceği olumsuzlukların da artarak devam edeceği açıktır. Bu büyük sorunu ortadan kaldırabilmek için en etkin ve akla yatkın çözüm yolu plastiklerin geri dönüşümüdür.

En yüksek tüketim oranına sahip plastik türlerinden biri olan polipropilen (PP), mükemmel kimyasal ve nem direnci, yüksek mekanik özellikler, düşük yoğunluk ve iyi işlenebilme gibi özelliklere sahiptir. Bununla beraber, PP' nin düşük darbe mukavemeti sebebiyle mühendislik plastiği olarak kullanımı ciddi anlamda kısıtlanmaktadır. Bu durum özellikle geri dönüştürülmüş PP hammaddeleri için daha büyük bir sorundur. Geri kazanım aşamasından önce yapısında meydana gelen termal ve oksidatif bozunmalar ve maruz kaldığı sıcaklık ve kayma gerilimleri mekanik özellikleri açısından çok daha yüksek kayıplara neden olmaktadır. Bu durum malzemenin kırılganlığına, mekanik ve yüzey özelliklerin kötüleşmesine, aynı zamanda kararlılığının azalmasına ve son ürün uygulamalarının sınırlanmasına sebep olmaktadır.

Bu çalışmada, geri kazanılmış PP'nin dayanıklılığını arttırmak, uygulama aralığını genişletmek ve özellikle otomotiv sektörü gibi yüksek darbe mukavemetinin büyük önem arz ettiği sektörlerde kullanımını yaygınlaştırmak amacıyla fonksiyonel katkılar kullanılmıştır. Bu amaçla, tek vidalı geri dönüşüm ekstrüderi kullanılarak granül haline getirilmiş üretim sonrası çocuk bezi ve ambalaj atıkları kullanılmıştır. Öncelikle geri dönüştürülmüş PP'nin darbe mukavemetini arttırmak amacıyla elastomerik katkı kullanılmıştır. Ancak, elastomer eklenmesi çekme mukavemeti,

elastisite modülü ve sertlik gibi mekanik özelliklerde kayıplara neden olmuştur. Elastomerik katkı kullanımının sebep olduğu bu dezavantajların önüne geçmek için çekirdeklendirici katkılar kullanılmıştır. "alfa (α)" tipi çekirdeklendirici katkılar ile PP'nin kristalizasyon davranışının değiştirilmesi hedeflenmiştir.Ayrıca proses iyileştirici olarak ikincil "antioksidan" kullanımı ile sinerjik bir etki gözlenmiştir.

Çalışmada örnekler, geri dönüştürülmüş PP'ye; %5 ve %10 oranında etilen- propilen dien monomer (EPDM); %0.5 oranında 3 farklı "α" tipi çekirdeklendirici katkı ve ikincil antioksidan katılarak eriyik karıştırma yöntemiyle hazırlanmıştır. Çift vidalı ekstrüder ile kullanılarak, elastomerik katkı, çekirdeklendirici katkı ve proses iyileştiricinin geri dönüştürülmüş PP üzerindeki etkilerini gözlemlemek amacıyla tekli, ikili ve üçlü katkı karışımları hazırlanmıştır. Ayrıca her bir karışımın hazırlanması sırasında numunelerin homojen görünümünü sağlamak amacıyla 3 phr oranında siyah masterbatch katkısı konulmuştur. Hazırlanan 24 adet numune enjeksiyon yöntemiyle ölçüm standartlarına (eriyik akış indeksi, çekme, darbe, sertlik testi çubuk ve plakaları) uygun basılıp bunların geri dönüştürülmüş PP'ye fiziksel, morfolojik, termal ve mekanik özelliklere etkileri incelenmiştir. Numunelerin fiziksel, morfolojik ve ısısal özelliklerinin belirlenmesi amacıyla yoğunluk, eriyik akış indeksi (MFI), X ışınları kırınımı (XRD), diferansiyel taramalı kalorimetre (DSC) ve polarize mikroskop (POM); mekanik özelliklerini belirlemek amacıyla çekme, darbe ve sertlik testleri yapılmıştır.

24 numunenin yoğunluk ölçümüne bakıldığında; farklı oranlarda EPDM, çekirdeklendirici ajan ve antioksidan içeren örneklerin yoğunlukları arasında fark olmadığı tespit edilmiştir. Numunelerin granülleri 230°C sıcaklıkta eritilerek üzerine 2.16 kg yük uygulanmıştır. EPDM katkısının oranı arttıkça malzemenin erime akış indeksinin düştüğü görülmüştür. Buna karşılık çekirdeklendirici ve antioksidan katkısının eriyik akış indeksini çok fazla etkilemediği gözlenmiştir. XRD sonuçlarına göre; çekirdeklendirici katkının kristalizasyon davranışı üzerindeki etkisi gözlenmiştir. α tipi çekirdeklendirici katkıların kullanımıyla monoklinik yapının işareti olan teta (θ) açısı ve şiddet değerleri elde edilmiştir.

DSC analizinde, numuneler oda sıcaklığı ile 300 °C aralığında 10 °C/dakika hız ile ısıtılmış ve soğutulmuştur. DSC analizi sonuçlarından çekirdeklendirici katkıların geri dönüştürülmüş PP'ye göre kristalizasyon sıcaklığını arttırdığı gözlenmiştir. DSC analizi sonuçlarına göre belirlenen erime ve kristalizasyon sıcaklık değerleri referans alınarak; numunelerin kristalizasyon davranışları, ısıtma düzeneği eklenmiş polarize mikroskop (POM) ile incelenmiştir. Isıtma düzeneği eklenmiş polarize mikroskop (POM) kullanılarak malzemenin kristalizasyon davranışının yanı sıra kristal yapı (spherulite) büyüme kinetiği video kaydıyla incelenmiştir. 250-110 °C sıcaklık aralığında 1°C/dakika soğutma hızıyla yapılan POM analizi esnasında, geri dönüştürülmüş PP'nin içerisine elastomerik ve çekirdeklendirici katkıların konulduğu tekli ve üçlü katkı karışımlarının kristalizasyon davranışları incelenmiştir. Çekirdeklendirici katkıların geri dönüştürülmüş PP'nin kristalizasyon sıcaklığını yükselttiği ve kristal yapılarınının (spherulite) boyutunu küçülttüğü görülmüştür.

Çekme deneyi sonuçlarına göre; tek başına EPDM katkısının ilavesiyle çekme mukavemetinin ve elastiklik modülünün düştüğü, böylece yüzde uzama değerinin arttığı görülmüştür. Ayrıca, çekirdeklendirici katkılar ve antioksidanın çekme mukavemetini ve modülü çok az oranda arttırdığı ve yüzde uzama değerini düşürdüğü görülmüştür. EPDM, çekirdeklendirici katkılar ve antioksidan, ikili karışımlarda etkilerini devam ettirmelerine rağmen; EPDM katkısının sebep olduğu bu dezavantajlar engellenememiştir. Ancak üçlü katkı karışımlarında sinerjik bir etki elde edilmiş ve çekme mukavemeti, elastiklik modülü, yüzde uzama değerlerinde beklenen sonuçlar görülmüştür. Çentikli Izod darbe testi sonuçlarına göre EPDM numunelerin darbe mukavemetini arttırmıştır. İkili katkı karışımlarında çekirdeklendirici katkı ve antioksidan, EPDM'in darbe mukavemeti üzerindeki pozitif etkisini düşürmüştür. Ancak üçlü katkı karışımlarında darbe mukavemeti oldukça artarak sinerjik bir etki elde edilmiştir. Shore-D sertlik testi sonuçlarına göre EPDM, çekirdeklendirici ajan ve antioksidanın aksine numunelerin sertliğini düşürmüştür.

1. INTRODUCTION

The recycling or recovering mean that is to againly win production processes of wastes, garbages or industrial wastages by using various recycling methods as raw material. Also; recycling is used as the symbol and name of saving methods all over the world. Energy-saving can be achieved with reusing of materials which may be recovered. An example about this situation must be given: Polypropylene is one of the most used plastic types, and while 77–85 MJ/Kg worth of energy is required for production of Polypropylene, 35–45 MJ/Kg worth of energy is required for production of Polypropylene by using recycling. In other words, 14000 kWh worth energy-saving can be achieved by using recovery of 1 tone of plastics. Besides, the amount of energy savings only in Turkey is 4 million Megawatt-hour (MWh). Thus, recycling technology which is developed for reducing waste burden of nature and using resources more effectively, is becoming more important day by day for plastic industry. [1]

Polypropylene (PP) is widely used for the production of plastic materials such as medical products, bottles, food containers, ducts, chemicals tanks, etc. It is a low cost material having good processability and high mechanical properties, which turns it to be an inexpensive material as compared to other polymer resin. It is the third most important plastic in the world from sale point of view. Its waste products are among the most visible in municipal waste due to its high volume to weight ratio and its chemically inert nature. Thus PP waste is perceived as a major problem. Besides its degradation during processing and application affects its properties. Degradation of PP is caused by heat, light, oxygen, humidity, etc. and these affect its chemical, optical, physical, and mechanical properties thus reduce its service life.

Presently, recycling of polymeric products is limited to certain materials only, so lots are still disposed off in a landfill or incinerated. In present society; the pressure for recycling of polymer waste is increasing with passage of time, since extraction of raw materials affects the environment, as well as reduces natural resources. It is very useful for our society to recycle polymeric materials to a greater extent to replace

virgin materials. But, it requires appropriate process and awareness about the properties of recycled polymeric materials, which lead to appropriate and useful application and increases the use of recycle materials. [2]

Polymer blending or compounding receives increasingly interest because it is a relatively easy way to obtain new materials with balanced properties. Generally, elastomers are used to improve the toughness but this situation sacrifices the modulus of polymers. Adding inorganic filler can enhance the stiffness but result in a decrease of toughness. To overcome the drawbacks resulted by only adding elastomer or filler, a lot of work has been done on polymer/elastomer/filler ternary system, where both elastomer and filler were used to enhance the toughness and stiffness simultaneously. To achieve the best combination of mechanical properties, the key is to control the dispersion and phase morphology of ternary composites. Concerning the phase morphology containing both elastomer and filler dispersed in polymer matrix, separated microstructure where the elastomer and filler are dispersed in polymer matrix separately, and core–shell microstructure with the filler covered the elastomer, are the two morphologies commonly observed in ternary composites. [2, 3, 5].

Although polypropylene (PP), one of the most versatile commodity and low-cost polymers, possesses excellent chemical and moisture resistance, good ductility and stiffness, low density, good processability; the potential of PP to be an engineering polymer has been seriously limited by its low impact resistance. In order to improve the impact toughness of PP and extend its application range, various works have been done on the toughening of PP by the incorporation of fine particles, particularly rubber particles of ethylene–propylene rubber and polyethelene-octene elastomer copolymer, etc. However, the rubber toughening strategy usually sacrifices the modulus and strength of PP. In recent years, to overcome the drawbacks caused by incorporation of rubbers only, much work has been done on ternary systems containing rubber and rigid inorganic fillers including calcium carbonate, silica, talc, etc., aiming at simultaneous reinforcing and toughening of the polymer matrixes. Nevertheless, the mismatching of properties such as miscibility of components, phase structure and phase size can affect the mechanical properties of the composite significantly. It is well known that PP is a semicrystalline and polymorphic material with several crystal modifications including monoclinic (α), hexagonal (β) and

orthorhombic (γ), etc. β form PP (β-PP) can be prepared with the aid of selective β-nucleating agent (β-NA) and exhibits higher heat distortion temperature and higher impact strength in comparison with a form PP (α-PP). [6]

Generally, the crystallization rate of semicrystalline polymers from the melted state depends on two factors: the nucleation rate and spherulites growth rate. Nucleating agent (NA) as one of the additives presents a role of increasing the nucleation density of polymer greatly and enhancing the nucleation rate dramatically, so that it has been widely used in semicrystalline polymers processing to reduce the cycle time and sometimes improve the optical properties of such polymers. It has been shown that the presence of NA affects the polymer nucleation activation energy and the fold surface energy. A good NA reduces the interfacial surface free energy. In a certain condition, the presence of NA also affects the lamellar thickness and the spherulites growth rates of polymers. [7]

The property profile of PP is strongly influenced by the level of crystallinity that is achieved when the polymer crystallizes from the melt. One class of additives known as crystal nucleating agents have a strong effect on both the level of crystallinity that is achieved, and the structure and morphology of these crystals. When molten polypropylene cools during extrusion or injection moulding, crystals begin to form at nucleation sites, which are often impurity particles. With time these crystals radiate outward from these nucleating centres forming spherical structures known as spherulites. Eventually the spherulites impinge on one another and the part becomes fully solid in nature. Since the spherulites scatter light, parts made from PP are typically translucent in nature, with poor see-through clarity. Amorphous (non-crystalline) material is also entrained within the spherulite, so that the overall crystallinity of the final part is somewhere in the range of 40-60% crystalline. The modulus (stiffness) and strength of the final part is dependent on the percent crystallinity, and higher crystallinity leads to higher stiffness and strength. One way of increasing the crystallinity is to increase the concentration of nuclei so that crystallization begins sooner and reaches a more complete state before the part has cooled to too low a temperature for additional crystals to develop. The introduction of more crystal nuclei dramatically speeds up the rate of crystallization, and this has the effect of reducing cycle time in injection moulding. Many nucleating agents have been developed to achieve these effects ranging from substances such as sodium

benzoate to the high performance organophosphate salts and sorbitol clarifiers. Certain high performance nucleators such as the sorbitols cause the spherulites to become much smaller than the wavelength of light, so that the light scattering is drastically reduced and clarity of the part is greatly improved. None of these traditional nucleating agents cause a change in the type of PP crystal that forms, and this crystal type is referred to as the alpha phase. Polypropylene can, however, develop into more than one crystal form. This property, known as polymorphism, is common to many substances. One of the most well known examples is carbon, which can crystallize as either graphite or diamond. Although the alpha crystal form is the most common one seen for PP, a second crystal form known as the beta form can develop if the proper nucleating agents are used. Certain nucleating agents have been found to produce the beta crystal form preferentially under the right processing conditions, and the following sections of this article explain some of the unique attributes of the beta crystal form, and how it can be used to produce a wide variety of products. [8]

In this study, recycled PP raw material, ethylene-propylene-diene-monomer (EPDM) with 5% and 10% ratio, 3 different grades of α-nucleated agent with 0.5% ratio and secondary antioxidant with 0.2% ratio were used to prepare samples. Mono, binary and ternary mixtures were prepared in order to oberve effects of elastomeric additive, nucleating agent and antioxidant on RPP by using melt mixing method with twin screw extruder.

2. THEORY

2.1 Recycling Technology and Plastics

Human activities produce waste of many kinds. “Municipal Solid Waste (MSW)” is defined as non-hazardous waste generated in households, commercial establishments and institutions; excluding industrial process waste, demolition waste, agricultural waste, mining waste, abandoned automobiles, ashes and sewage sludge. Waste management can in a narrow sense be defined as “how to get rid of the trash“ but a broader definition also includes issues such as:

- How to re-appraise materials previously considered as waste, by setting up in-house recycling schemes.
- How to realise, and possibly also increase, the value of materials that is waste to us but may be regarded as a resource by others.
- How to delay the point in time at which a product becomes waste by extending its lifetime or by re-use.
- How to prevent materials from becoming waste by reducing material consumption through modified designs and technology.

The plastic fraction of MSW can’t be discussed in isolation from MSW management in general because it is only a minor fraction of the total MSW. This means that any special arrangements regarding the plastic fraction will be associated with considerable costs, but also potential benefits. An illustration of the interdependence of plastic waste management with waste management in general is that, if incineration with energy recovery is the dominant method, it is likely to be attractive not to sort out the plastic fraction for mechanical recycling. The reason is that plastics have a high fuel value. If, on the other hand, landfilling is the prevalent method, separate recycling schemes for plastics will be more attractive because plastic waste generally has a high specific volume. [9]

2.2 Recycling Rates in the Europe and World

In the EU27, 503 kg of municipal waste was generated per person in 2011, while 486 kg of municipal waste was treated per person. This municipal waste was treated in different ways: 37% was landfilled, 23% incinerated, 25% recycled and 15% composted, compared with 56% landfilled, 17% incinerated, 17% recycled and 10% composted in 2001.

The amount of municipal waste generated varies significantly across Member States. Denmark, with 718 kg per person, had the highest amount of waste generated in 2011, followed by Luxembourg, Cyprus and Ireland with values between 600 and 700 kg per person, and Germany, the Netherlands, Malta, Austria, Italy, Spain, France, the United Kingdom and Finland with values between 500 and 600 kg. Greece, Portugal, Belgium, Sweden, Lithuania and Slovenia had values between 400 and 500 kg, while values of below 400 kg per person were recorded in Hungary, Bulgaria, Romania, Latvia, Slovakia, the Czech Republic, Poland and Estonia.

Recycling most common in Germany, incineration in Denmark and composting in Austria. The treatment methods differ substantially between Member States. In 2011, the Member States with the highest share of municipal waste landfilled were Romania (99% of waste treated), Bulgaria (94%), Malta (92%) and Latvia (88%).

The highest shares of incinerated municipal waste were observed in Denmark (54% of waste treated), Sweden (51%), Belgium (42%), Luxembourg and the Netherlands (both 38%), Germany (37%), France and Austria (both 35%).

Recycling was most common in Germany (45% of waste treated), Ireland (37%), Belgium (36%), Slovenia (34%), Sweden (33%), the Netherlands (32%) and Denmark (31%). The Member States with the highest composting rates for municipal waste were Austria (34%), the Netherlands (28%), Belgium and Luxembourg (both 20%), Spain and France (both 18%).

Recycling and composting of municipal waste together accounted for more than 50% of waste treated in Germany (63%), Austria (62%), the Netherlands (61%) and Belgium (57%). [10]

Table 2.1 : Municipal waste, 2011[10]

	Municipal waste generated, kg per person	Total municipal waste treated, kg per person	Municipal waste treated, %			
			Landfilled	Incinerated	Recycled	Composted
EU27	**503**	**486**	**37**	**23**	**25**	**15**
Belgium	465	460	1	42	36	20
Bulgaria	375	371	94	0	3	3
Czech Republic	320	319	65	18	15	2
Denmark	718	718	3	54	31	12
Germany	597	597	1	37	45	17
Estonia	298	257	70	0	20	10
Ireland	623	580	55	5	37	4
Greece	496	496	82	0	15	3
Spain	531	531	58	9	15	18
France	526	526	28	35	19	18
Italy	535	505	49	17	21	13
Cyprus	658	658	80	0	11	9
Latvia	350	292	88	0	10	1
Lithuania	442	432	79	1	19	2
Luxembourg	687	687	15	38	27	20
Hungary	382	382	67	11	17	5
Malta	584	536	92	1	7	0
Netherlands	596	502	1	38	32	28
Austria	552	528	3	35	28	34
Poland	315	255	71	1	11	17
Portugal	487	487	59	21	12	8
Romania	365	293	99	0	1	0
Slovenia	411	351	58	2	34	6
Slovakia	327	312	78	11	5	6
Finland	505	505	40	25	22	13
Sweden	460	460	1	51	33	15
United Kingdom	518	514	49	12	25	14
Iceland	571	530	73	11	14	2
Norway	483	473	2	57	25	15
Switzerland	689	689	0	50	35	16
Croatia	373	371	92	0	8	1
Former Yug. Rep of Macedonia	357	357	100	-	-	-
Serbia	361	281	100	0	0	0
Turkey	395	333	99	0	0	1
Bosnia and Herzegovina	410	391	100	-	-	-

2.3 Recycling Steps and Plastic Wastes

Usage of plastics is growing severely day by day; facing countries, especially industrialized ones with the big trouble of plastic waste. Proper disposal of the waste has made social and environmental arguments. Increased use of plastics is due to good surface characteristics and appearance, light weight, strength and low cost of them [11].

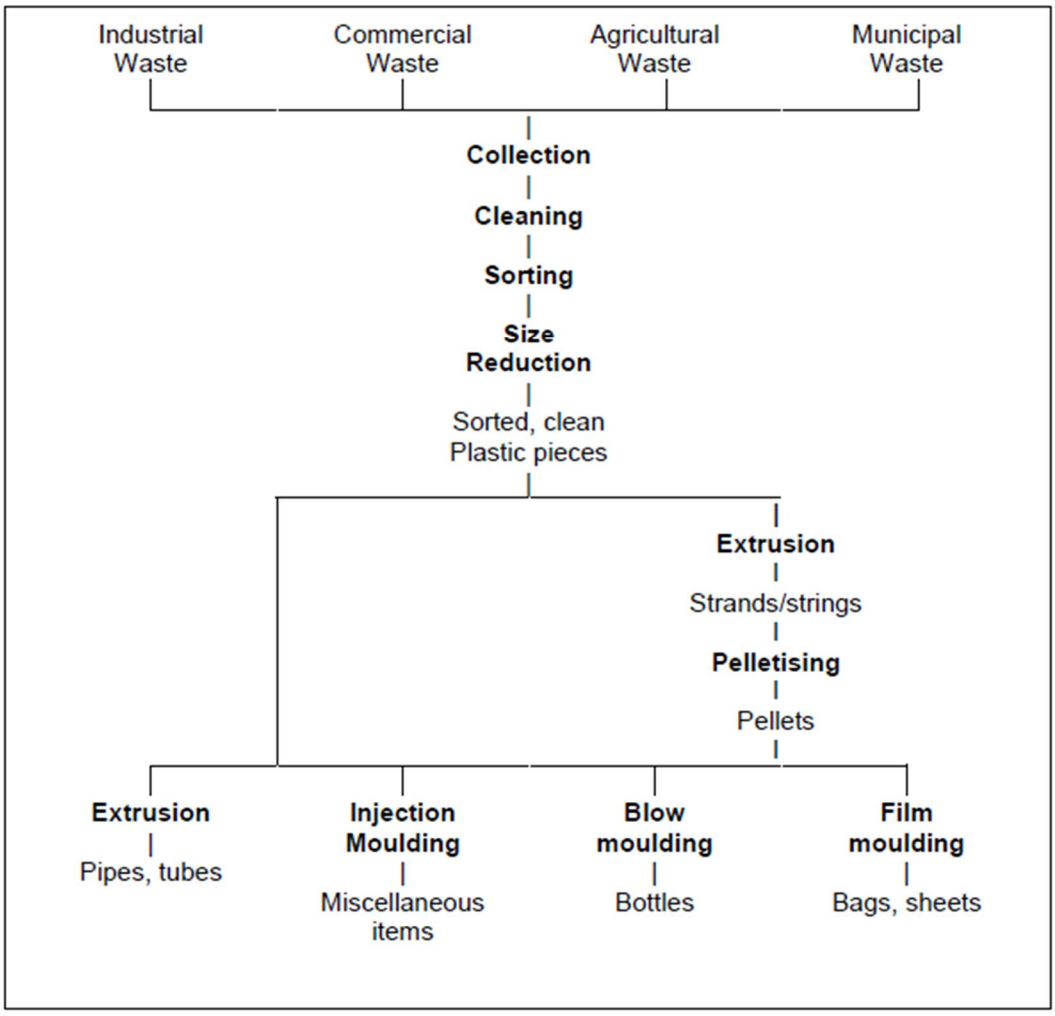

Figure 2.1 : Steps of recycling [13]

No doubt that an integrated waste management approach is needed to handle plastic wastes that are so big in volume, being mixtures of various types of plastics and also contains some kinds of contamination. Efficient disposal, recycling and use of material, energy and environment considerations must be determined carefully. Therefore different steps of plastics background such as manufacturing processes, co-existing raw materials, design and fabrication of the finished products, possible

reuse of each item, and the proper disposal of the wastes have been studied to build up this waste management model. Such model comprises of:

- Source reduction
- Reuse
- Recycling
- Landfill
- Waste-to-energy

The historically most common method for dealing with MSW, including plastic waste, is deposition in landfills. In areas with a high population density such as Western Europe, North-Western USA and Japan, landfilling is becoming more and more difficult and expensive because locations suitable for such a purpose are scarce. An alternative approach to landfilling that has been proposed is the establishment of strategic storage facilities.[9]

Recycling and incineration (waste-to-energy) are the usual focused aspects of recovery methods. Heat recovery method for plastics waste incineration comes along with production of toxic gases (due to the existence of PVC) and toxic fly; and residue ash contains lead and cadmium. Also form energy saving point of view, plastic incineration is a low efficient technique.

Recycling is a choice to deal with such problems, to manage the plastic wastes, to reduce the environmental problems as much as possible and to save the resources. Ideally the best way to minimize the amount of wastes and reduce the consumption of fossil fuels is recycling; that also saves both material and energy since recycling of the plastics uses less energy rather than new virgin resin production and the recycled plastics strongly compete with the virgin resins.

Recycling of plastics consists of four steps:

- Collection
- Separation
- Processing
- Marketing

To have a better quality of the recycled plastic, different types of polymers have to be separated from each other in the collected plastics waste. The material which is made by a mixed plastic waste recycling has a low quality (such as low mechanical stability) in comparison with the new virgin resins. So, an efficient system for mixed post-consumer plastic waste separation is needed.

2.3.1 Plastic waste classification and types

Materials which have reached their end of life, and must therefore be discharged and materials which remain from production consist as waste. One part of this term is plastic waste. Plastic wastes are divided into two groups; municipal plastic wastes (MPW) and industrial plastic wastes. Five major types of plastic are the most constitutive parts of the municipal waste volume in Europe. These types are: polyethylene (as low and high density polyethylene, (HDPE and LDPE)), polypropylene (PP), polystyrene (PS) polyethylene terephthalate (PET) and polyvinyl chloride (PVC). Besides PET and PVC, POM (polyoxymethylene) are also categorized in the engineering plastic waste [11].

Figure 2.2 : Types of plastic wastes [1]

Industrial waste (or primary waste) can often be obtained from the large plastics processing, manufacturing and packaging industries. Rejected or waste material usually has good characteristics for recycling and will be clean. Although the quantity of material available is sometimes small, the quantities tend to be growing as consumption, and therefore production, increases.

Municipal waste can be collected from residential areas (domestic or household waste), streets, parks, collection depots and waste dumps. In Asian cities this type of waste is common and can either be collected from the streets or can be collected from households by arrangement with the householders.

Figure 2.3 : Plastic wastes

2.3.2 Collection and sorting

In general RPP which is going to be processed in recycling facilities is collected in two ways, post-product and post-consumer. In both ways, it generally contains 5% polyethylene and some inorganic additives. This RPP is processed as downcyle or repurposed by mixing with some amounts of virgin PP. RPP quality is important for reusing and mixing with virgin PP is essential. On the other hand, upcycling means

improving the quality of the used articles by increasing their value and obtaining new usage areas with high added-value

Several techniques can be used to separate mixed plastic wastes based on their physicochemical properties. But some of them have their own limitations. Some of the separation methods are mentioned below with a brief explanation:

Gravity separation; that is based on plastic types and density. therefore separation of close density plastics (such as mixture of PVC, PET and POM) could be very difficult.

Contact charging (triboelectrification); where separation is mainly carried out upon the difference in dielectric constant of plastics.

- Hydrocyclones and centrifuges, this is another method based on the differences in plastic density.
- Froth flotation; this technique is one of the techniques widely used in mineral industry but is either adopted for industrial applications. Froth flotation is the main and the most efficient method for separation which is based on the surface properties of plastics.

Manual sorting can be used besides the all above separation methods suffering some major disadvantages such as being very labour-intensive and their high cost. Also it would be hazardous for the labours. [11]

When thinking about setting up a small-scale recycling enterprise, it is advisable to first carry out a survey to ascertain the types of plastics available for collection, the type of plastics used by manufacturers (who will be willing to buy the reclaimed material), and the economic viability of collection.

The method of collection can vary. The following gives some ideas;

- House to house collection of plastics and other materials (e.g. paper).
- House to house collection of plastics only (but all types of polymer).
- House to house collection of certain objects only.
- Collection at a central point e.g. market or church.
- Collection from street boys in return for payment.

- Regular collection from shops, hotels, factories, etc.
- Purchase from scavengers on the municipal dump.
- Scavenging or collecting oneself.

The method will depend upon the scale of the operation, the capital available for set-up, transport availability, etc. The standard EN 15347 classifies types of plastic waste material. A major challenge in producing recyclate is that most plastic types are inherently immiscible at the molecular level and have different processing requirements. When plastic is contaminated, in limited quantity or with a varied composition, recycling is more difficult. The cleaner and the fewer different types of plastic, the less mechanical treatment is required and the higher the quality of the recycled plastic products.

Sorting and separation thus affect the cost of recycling and the quality of recyclate. Indeed, sorting plastic waste at an early stage may be the most significant activity in the recycling loop, raising the quality of the waste by grouping types and colours. The sorting process first separates plastics from fibres, then films from other plastics, then PVC, PP, PS etc. from PE. Automatic sorting techniques have emerged and are becoming more widespread, though manual sorting is still used by some recycling facilities. Automatic techniques are continuously being improved; the most common currently is near-infrared detection. Efficient collection and sorting enables high quality recycling. By increasing the value of waste, the recycling sector in turn makes collection schemes more economically feasible.

2.4 Recycling of Plastics

Most plastics in use today are thermoplastics, which means that the material can be melted and reshaped. Some plastics are thermo-sets, which means that they cannot be melted without severe chemical degradation. This makes the possibilities of recycling of thermo-sets very limited.

Most thermoplastics are highly suitable for recycling, at least in theory. Numerous studies have shown that the important properties of the most common plastics are fairly well preserved throughout several cycles of processing and ageing. This means that any company that puts products on the market that are made of thermoplastics can claim that its products are recyclable. For it to become realistic that the material

will be recovered and recycled, several other criteria must however be fulfilled. There has to be an infra-structure available for collecting, sorting and reprocessing the material and there have to be useful applications for the material in its second life.

Recycling infrastructures are characterised by the requirement of economy of scale. This means that large amounts of material have to be recovered in order to sustain the system for recycling. A plastic product is consequently not in practice recyclable unless there is enough discarded material of the same kind to make recycling worthwhile. A possible strategy to overcome this dilemma is to recycle waste plastics as "commingled plastics", which means that the plastics are reprocessed without prior sorting according to plastic type. Park-benches, poles and fences are examples of products that are being made out of commingled plastics. The value of materials made out of commingled waste plastics is very low compared to that of virgin plastics and this type of recycling is therefore sometimes referred to as "down-cycling" [9]

"Upcycling" is an alternative to recycling or downcycling. Upcycling occurs when something of little value is turned into something of better quality and greater value. Upcycling has many creative uses from art to design to consumer goods. Artists and designers in the developed world have caught onto this idea and have come up with some creative ways to use plastic bags as well as other "trash." [12]

In 'western' countries, plastic consumption has grown at a tremendous rate over the past two or three decades. In the 'consumer' societies of Europe and America, scarce petroleum resources are used for producing an enormous variety of plastics for an even wider variety of products. Many of the applications are for products with a life-cycle of less than one year and then the vast majority of these plastics are then discarded. In most instances reclamation of this plastic waste is simply not economically viable.

In industry (the automotive industry for example) there is a growing move towards reuse and reprocessing of plastics for economic, as well as environmental reasons, with many praiseworthy examples of companies developing technologies and strategies for recycling of plastics.

Not only is plastic made from a non-renewable resource, but it is generally non-biodegradable (or the biodegradation process is very slow). This means that plastic litter is often the most objectionable kind of litter and will be visible for weeks or months, and waste will sit in landfill sites for years without degrading.

Although there is also a rapid growth in plastics consumption in the developing world, plastics consumption per capita in developing countries is much lower than in the industrialised countries. These plastics are, however, often produced from expensive imported raw materials. There is a much wider scope for recycling in developing countries due to several factors:

- Labour costs are lower.
- In many countries there is an existing culture of reuse and recycling, with the associated system of collection, sorting, cleaning and reuse of 'waste' or used materials.
- There is often an 'informal sector' which is ideally suited to taking on small scale recycling activities. Such opportunities to earn a small income are rarely missed by members of the urban poor.
- There are fewer laws to control the standards of recycled materials. (This is not to say that standards can be low – the consumer will always demand a certain level of quality).
- Transportation costs are often lower, with hand or ox carts often being used.
- Low cost raw materials give an edge in the competitive manufacturing world.
- Innovative use of scrap machinery often leads to low entry costs for processing or manufacture.

In developing countries the scope for recycling of plastics is growing as the amount of plastic being consumed increases.

Two methods of recycling are used commonly, mechanical recycling and chemical recycling. Plastic recycling process consists of two essential and necessary steps. One is an automatic identification tool for sorting the plastics and the other is characterization of the regenerated products. The former is due to the fact that recycling of a mixed plastic waste makes a product with inadequate and poor

properties. And the later is due to information about the quality of the regenerated product which has to be delivered to the end user.

2.4.1 Chemical recycling

The other recycling method, chemical or feedstock recycling can be used with mechanical recycling as a complementation. In this procedure the polymers are chemically converted to monomers through a chemical reaction. These monomers then can be used for new polymerizations to reproduce the original or a related polymeric product. [11]

The degradation of polymeric materials into low molecular weight compounds is referred to as feedstock recycling or chemical recycling. The ideal form of feedstock recycling is to convert the polymer back to monomers that can be purified using normal chemical methods and then repolymerised, yielding a material that is identical to virgin resin. This is technically possible for condensation polymers such as PET and polyamides. For plastics such as polyethylene and polypropylene there is no technique available that gives a particularly high yield of monomer, but it is possible to produce fuel oils and synthesis gases by pyrolysis. [9]

Chemical recycling is a burden some method that needs a lot of investment and expert personnel; so it is not developed completely yet and only a few companies work on it. Some chemical reactions used for decomposition of polymers into monomers are:

- Glycolysis
- Pyrolysis
- Ammonolysis
- Hydrogenation
- Hydrolysis
- Gasification
- Cracking
- Methanolysis [11]

2.4.2 Mechanical recycling

Mechanical recycling is a physical method, in which the plastic wastes will be formed into flakes, granulates or pellets of appropriate quality for manufacturing, where they would be melted to make the new product by extrusion. The best results would be for plastic wastes which contain just one kind of polymer, mechanical recycling is the better method for recycling. The process usually consists of contaminants removal, grinding or conversion into flakes and pellets, washing, drying and melting [11].

Mechanical recycling refers to both primary and secondary recycling. The processing of plastics often generates a considerable amount of production scrap. The mechanical recycling of such material, i.e. material that has not been converted to a useful product, is referred to as primary recycling. Examples of such plastic material that can be re-utilised are edgetrims, start-up and change-over scrap, finished products or parts that fails to meet required standards, material solidified in mould runners, etc. Primary recycling can be done in-house if the necessary equipment is available. Machines used for primary recycling are shredders, grinders and extruders. The recycled material is often mixed with virgin resin and fed back into the same process that generated it, but it is also possible to produce other products. If a plastic processing industry does not recycle production scrap itself, the material can be sold to other companies for primary recycling. This solution may be attractive to processors who cannot afford to invest in the necessary recycling equipment. To sell production scrap on the open market can however be risky, since it may make it possible for competitors to acquire cheap raw-materials and thereby gain a competitive advantage. Secondary recycling is what we normally think of when the recycling of plastics is mentioned, i.e. the reprocessing of material from used, discarded products into new products. [9]

Initial upgrading: Once the plastic has been collected, it will have to be cleaned and sorted. The techniques used will depend on the scale of the operation and the type of waste collected, but at the simplest level will involve hand washing and sorting of the plastic into the required groups. More sophisticated mechanical washers and solar drying can be used for larger operations. Sorting of plastics can be by polymer type

(thermoset or thermoplastic for example), by product (bottles, plastic sheeting, etc.), by colour, etc.

Size reduction techniques:_Size reduction is required for several reasons; to reduce larger plastic waste to a size manageable for small machines, to make the material denser for storage and transportation, or to produce a product which is suitable for further processing. There are several techniques commonly used for size reduction of plastics. For example; cutting is usually carried out for initial size reduction of large objects. It can be carried out with scissors, shears, saw, etc. Shredding is suitable for smaller pieces. A typical shredder has a series of rotating blades driven by an electric motor, some form of grid for size grading and a collection bin. Materials are fed into the shredder via a hopper which is sited above the blade rotor. The product of shredding is a pile of coarse irregularly shaped plastic flakes which can then be further processed. Agglomeration is the process of pre-plasticising soft plastic by heating, rapid cooling to solidify the material and finally cutting into small pieces. This is usually carried out in a single machine. The product is coarse, irregular grain, often called crumbs.

Further processing techniques: Extrusion and pelletising. The process of extrusion is employed to homogenise the reclaimed polymer and produce a material that it subsequently easy to work. The reclaimed polymer pieces are fed into the extruder, are heated to induce plastic behaviour and then forced through a die (see the following section on manufacturing techniques) to form a plastic spaghetti which can then be cooled in a water bath before being pelletised. The pelletisation process is used to reduce the ‘spaghetti’ to pellets which can then be used for the manufacture of new products [13].

Recycling of plastic waste almost always refers to mechanical recycling, which is the processing of waste plastics by physical means (grinding, shredding, washing, drying and melting) back into plastic products. The “efficiency” of this process for a given amount of plastic varies but 60% on average can be used as a rough estimate. The remaining 40% cannot be recycled and ends up as waste (side products) that can be sent for energy recovery, reuse by other industries or, as a last resort, to landfill. If the collection and sorting of plastics waste improves, the efficiency of recycling lines will also increase.

Around 3,2 Mt of post-consumer plastic is recycled in Europe. The final recycling output is thus around 1,9 Mt (60%). By way of comparison, that amount of output could only meet around two weeks of plastics demand if the supply of virgin plastics dried up: in 2011, demand for plastics in Europe was 47 Mt or 0,9 Mt per week. Recycling currently only meets around 4% of demand.

Bio-based plastics (i.e. those derived from renewable sources) are generally not a problem for mechanical recycling as they are designed to keep their properties. Biodegradable plastics on the other hand, lose their properties and create a lower melt flow index (i.e. the degradation of the organic part), which lowers the quality of the recyclate. Greater penetration of biodegradable products in non-biodegradable plastic streams is thus a threat to plastics recycling.

The alternatives to recycling for treatment of plastic waste are energy recovery (incineration) and landfill. Incineration capacity is quite high in the EU – around 8,6 Mt currently goes to energy recovery. Significant amounts of energy can be recovered from plastics for use in heating or power generation but ideally energy recovery should be reserved for non-recyclable materials.

2.5 Nucleating Agents and Crystallization Behaviour

2.5.1 Crystallization of polymers

Crystallization of polymers is a process which is responsible to the formation of a new crystalline phase. It occurs within the cooling polymer at the so-called nuclei upon lowering the polymer's temperature below its melting temperature. This process consists of several stages of nucleation and growth. There are essentially two major types of nucleation in polymers: homogeneous and heterogeneous.

The homogeneous nucleation which is characterized by a constant rate of nucleation stems from statistical fluctuations of the polymer chains in the melt. The heterogeneous nucleation, on the other hand, is characterized by a variable rate and a relatively low supercooling temperature. This occurs in the presence of foreign bodies which are present in the polymer melt and which increase the rate of crystallization, acting as alien heterogeneous nuclei and reducing the free energy for the formation of a critical nucleus.

When semi-crystalline polymers crystallize from the melt (typically during the cooling phase of a process), the lamellae organize from a primary nucleus to form complex macro-structures called spherulites. It is widely known that these spherulites continue to grow until they impinge on an adjacent spherulite at which point the growth ceases. The ultimate size of these spherulitic structures dictates a number of properties of the polymer, including optical and physical characteristics. Additionally, for crystal growth to commence there is a primary process that has to occur, called nucleation; this is basically the formation of a focal center around which the lamellae can organize themselves. This process is displayed in Figure 2.6 The secondary process of crystal growth follows nucleation and is characteristic for polyolefins.

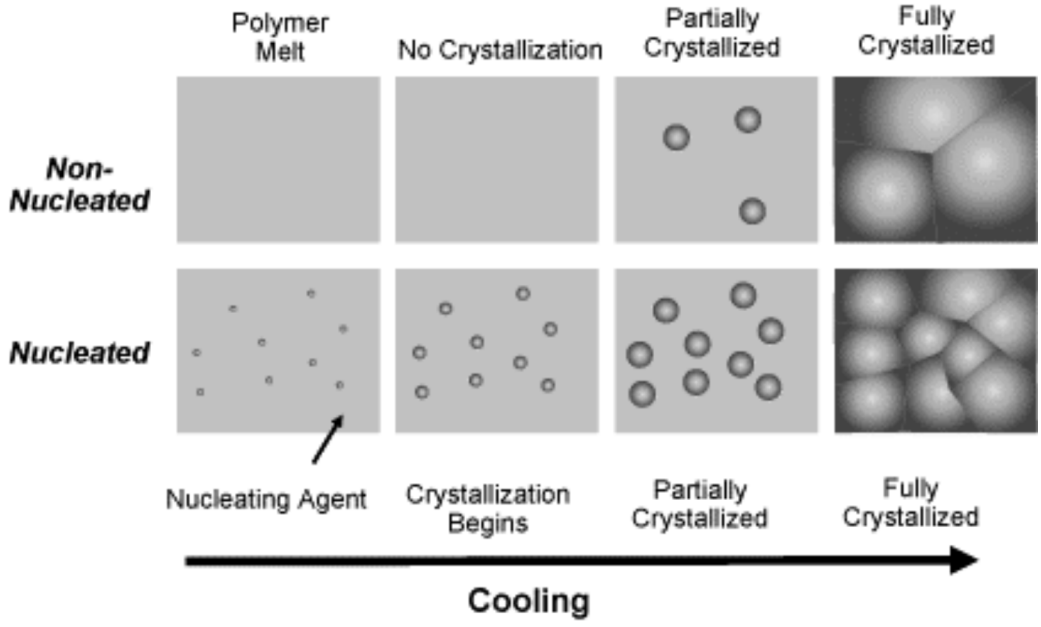

Figure 2.4 : Effect of nucleating agents on polyolefins [15]

From thermodynamic considerations alone, a crystal is in a lower free energy state than the liquid when the temperature is below the melting point for a large crystal of a very high molecular weight polymer. Crystallization adheres to Gibbs free energy :

$\Delta G=\Delta H-T\Delta S$,

where ΔG is change in free energy, ΔH is change in enthalpy, T is temperature and ΔS is change in entropy.

When ΔG is:

negative → crystallization proceeds spontaneously;

zero → system is at equilibrium;

positive → crystallization will not proceed. [15]

2.5.2 Polypropylene Crystallization

As polypropylene (PP) cools from the molten state, individual chains begin to form crystalline structures around nucleation sites. These nucleation sites can either be imperfections or inconsistencies in a polymer chain or foreign particles in the melt. As the polymer continues to cool, more chains crystallize around the nucleation site, forming spherulites. When PP cools completely, it is made up of approximately 60% crystalline and 40% amorphous, or non-crystalline, areas. The crystallization rate of PP is increased by the presence of foreign particles in the melt around which the polypropylene chains can crystallize.

While it is cooling, PP also undergoes supercooling. Supercooling refers to the difference between the melting temperature and the temperature at which crystallization of the polymer begins. This temperature is called the "onset of crystallization temperature." For example, PP random copolymers (without a nucleating agent) melt at about 145°C (293ºF) but begin to crystallize at about 112°C (234°F). This temperature difference means that molded parts must be cooled well below the melting point of PP before the resin begins to crystallize.

Nucleating agents (nucleators) and clarifying agents (clarifiers) work by altering the way the PP chains crystallize and agglomerate in the molten state. Nucleators and clarifiers also reduce the degree of supercooling in the resins by increasing the onset of crystallization temperature. These agents provide numerous nucleating sites around which the PP chains can crystallize. The numerous nucleating sites also increase the amount of crystallinity in the resin and decrease the average size and narrow the size range of the spherulites. Nucleators and clarifiers also increase the stiffness of the end product and slightly reduce the impact strength.

Nucleating agents are generally inorganic materials with a small average particle size and a high melting point. When a nucleated resin is melted in an extruder, the nucleating agent remains solid and provides a site around which the PP spherulites can form.

The most effective nucleating agents are chemical derivatives of benzoic acid. Because of its strong nucleating ability and low cost, the most widely used nucleating agent is sodium benzoate, a synthetic, white, opaque powder. Other nucleating agents include naturally occurring minerals such as kaolin and talc.

Adding a nucleating agent to PP increases crystal growth, and this growth occurs faster and at a higher temperature (15 to 20°C) than without the additive. Because the degree of supercooling is reduced, parts made from nucleated PP resins can be removed from the mold at higher temperatures and as a result, cycle times are decreased and output raised.

However, in multi-cavity and thin-wall injection molds, nucleating agents may cause the resin to solidify before the mold cavity is completely filled, resulting in short shots. Another potential downside is that sodium benzoate is known to interfere with red pigments, causing them to turn orange. Nucleating agents are also not typically used to stiffen random copolymer PP resins because clarity decreases. [14]

Polypropylene can exist in different morphological forms, depending on the tacticity of the resin and the crystallization conditions, such as pressure, temperature and cooling rate. Different form can co-exist and one polymorphic form can change into another as conditions changes. The effects of these structures can be observed by using Polarizing microscope (POM); and can be calculated by using Dynamic mechanical analysis (DMA). There are three modifications:

α-phase (monoclinic): Polymer chains in the α-form of isotactic polypropylene form a helical structure in the monoclinic unit cell. Lamellae thickness is 5–20 nm. Radial growth of lamellae is dominant; however lamellae can also associate tangentially, with the tangential lamellae branching of approximately orthogonally from the plane of the radial lamellae. The α-form is the primary form of polypropylene obtained under normal processing conditions.

β-phase (hexagonal): The β-form of isotactic polypropylene has a hexagonal unit cell structure (or according to Varga trigonal unit cell), with more disorder than the α-form. Polypropylene can crystallized in the β-form at specific crystallization conditions, mainly in the presence of specific nucleating agents.

γ-phase (orthorhombic): The γ-form of isotactic polypropylene was initially considered to have a triclinic unit cell with dimensions similar to the α -form, but the

crystal structure was recently reassigned as an orthorhombic unit cell with nonparallel, crossed lamellae. The γ-form develops under high pressure of 200 MPa.

Each of the forms of iPP possesses different physical properties. The most thermodynamically stable α-form has the highest melting temperature and E-modulus, while β-form has significantly improved impact strength and drawability.[15]

2.5.3 Nucleating agents

Nucleating agents are chemical substances which when incorporated in plastics form nuclei for the growth of crystals in the polymer melt. In polypropylene, for example, a higher degree of crystallinity and more uniform crystalline structure is obtained by adding a nucleating agent such as adipic and benzoic acid or certain of their metal salts. Generally, three classes of nucleating agents can be distinguished:

- conventional nucleating agent;
- advanced nucleating agent;
- hyper nucleating agent.

The heterogeneous nucleation is also profitably applied to improve clarity of the material. Such nucleating agents are called clarifying agents and they dramatically decrease the opacity of the polymer. For example, common clarifying agent used in Polypropylene is based on 1,3;2,4-bis(3,4-dimethylbenzylidene)sorbitol.

Conventional nucleating agents are the oldest nucleating agents. The most commonly used even until today are talc, sodium benzoate and aromatic carboxylic acid salts. Fillers such as talc usually induce α form in iPP, however many organic agents also can promote the formation of α and β-form. In some industrial application talc is preferred for its low cost. Usage of talc brings about several modifications of polypropylene properties, which increase the industrial interest for this particular composite. Advanced nucleating agents are known since 1980s and it is a newer class of nucleating agents. These have since become widely used in copolymer resins that require additional modulus enhancement and faster crystallization. Most important among these advanced nucleating agents are the phosphate ester salts.

Hyper nucleating agents are the most recently developed and offer processors and users the combined benefits of high crystallization rates and isotropic shrinkage control which lead to improved production and part quality performance, in addition to the traditional mechanical property-related enhancements. Hyper nucleation technologies can also be combined to find the appropriate balance of dimensions and properties. Thus, this newest class of hyper nucleation technologies combines the main benefits of traditional nucleators whilst further optimizing performance and thus broadening the use window of polypropylene and polyethylene [15].

2.5.4 Nucleating agents for polypropylene

Application of nucleating agent in polypropylene is, together with shortening of processing time, traditionally used to improve physical properties and, in the case of some α-NAs called clarifying agents, dramatically improve aesthetics of PP. Nucleating agents for polypropylene are generally divided into two groups: α - nucleating agent causing the crystallization into α-phase and β-NA for inducing formation of trigonal β-phase. The typical α-NAs consist of sodium benzoate, kaolin or talc. The β-NAs are for example triphenodithiazine, pimelic acid with calcium stearate and so on.

The most common α-NAs are sorbitol based derivates. Sorbitol based nucleators provide significant improvement over conventional nucleating agents both in nucleating efficiency and clarity. Unlike the dispersion type nucleators, they dissolve in the molten iPP and disperse uniformly in the matrix. When the iPP cools, the nucleator first crystallizes in the form of a three-dimensional fibrillar network of nanometric dimensions. The fibrils serve as nucleating sites for iPP, probably due to epitaxial growth. The most common examples of this type of nucleators are:

- 1,2,3,4-bis-dibenzylidene sorbitol (DBS)
- 1,2,3,4-bis-(p-methoxybenzylidene sorbitol) (DOS)
- 1,2,3,4-bis-(p-methylbenzylidene sorbitol) (MBDS)
- 1,3;2,4-di-(3,4-dimethylbenzylidene sorbitol) (DMDBS)

In melt-crystallized material the predominant polymorph is α-form (monoclinic). The β-form (trigonal) generally occurs at levels of only a few percent, unless certain

heterogeneous nuclei are present or the crystallization has occurred in a temperature gradient or in the presence of shearing forces. β-crystals have a melting point that is generally 10-15 ^{o}C lower than that of α-crystals [15].

2.6 Literature Survey

Incarnato and co-workers analyzed the effect of many recycling operations on the rheological and mechanical properties of a commercial polypropylene (PP) extruded up to seven times. The polymer, recycled several times, was also used to prepare binary mixtures with various percentages of virgin PP. Mechanical analysis of single component films has shown a drop in the elongation at break with the increase of recycling operations. They promotes that this behaviour is strictly dependent upon the molecular structure ($M_{w,}$ MWD) of the polymer and upon the morphology (orientation, crystallinity) of the films. Besides, the tensile properties of the blend films have revealed that is possible to add an high percent age (70% w/w) of recycled polypropylene without a significant reduction of the mechanical performance of the PP films [16].

Yang and co-workers studied the variation of toughness and other mechanical properties of the toughened systems aroused by the introduction of β-TPVs. The performance differences of the toughened systems were compared. The crystalline structures, phase morphology of the toughened systems were investigated and the relationships between phase structure and toughness of PP/β-TPVs blends were discussed. According to results of this study; β crystals of PP were efficiently induced by β-NA in β-TPVs toughened PP blends. As the content of β-NA increased, the content of the β crystals in corresponding PP/β-TPVs blends increased, and the impact toughness of the PP/β-TPVs blends also increased accordingly. A synergic toughening of TPV particles and β crystal of PP has been proposed [17].

Jacoby mentioned about commercial nucleating agents. According this paper; at present there are only a handful of nucleating agents taht preferentially nucleate the beta crystal phase. Although there are many commercially available grades of alpha nucleated polypropylene, there are almost no commercially available beta nucleated PP grades. This situation has limited the numner of commercial applications of beta nucleated polypropylene. They developed beta nucleant masterbatches that can be added to non-nucleated PP. Jacoby emphasised the importance of nucleating agent

effect in terms of crystallization and mechanical properties such as stiffness and strength on PP in the paper and presentation [18,19].

Jacoby studied about beta nucleation effect on Polypropylene. 1st-generation and 3rd-generation beta masterbatches were used and the larger size of the beta melting peak and higher T_c (crystallization temperature) values from the DSC diagrams by using heating and cooling at a rate of 10°C per minute. Beta masterbatches were compared in terms of T_c and the size of melting peak [20].

Xin and co-workers studied about crystallization kinetics of iPP nucleated with α/β compounded NAs. They selected three kinds of well studied α/β compounded NAs, Phosphate/Amide, Sorbitol/Amide, and Phosphate/Carboxylate, to review. When Isothermal and non-isothermal crystallization kinetics of iPP nucleated by three kinds of α/β compounded NAs were reviewed, they deduced compounded NAs will increase the crystallization temperature of iPP, shorten the crystallization halftime. Consequently the molding cycle time of iPP will be reduced obviously, which has great importance for polymer processing. Besides, they investigated crystallization morphologies of iPP nucleated with α/β compounded NAs. According to Polarized optical microscope results the size of spherulites in nucleated iPP appeared much smaller than that of in pure iPP. However, iPP nucleated by different NAs showed different crystallization morphologies [21].

Bai and co-workers studied nonisothermal crystallization behaviors, crystalline structures, and subsequent melting behaviors of PP nucleated by individual or compounded NAs. During experimental, they used various types of nucleating agents and they investigated morphological properties. Their results show that the crystallization of PP nucleated with compounded NAs is greatly dependent on the composition, especially nucleating agent content [22].

Luo and co-workers implemented a comparative investigation between adding α or β nucleating agent (α-NA or β-NA) to tailor the toughness of impact polypropylene copolymer (IPC) among test temperatures, 23º and -15°C. By carefully correlating the polymorphic composition, chain mobility of matrix amorphous portion and multiphase morphology to toughness, the physical origin of the toughening behavior observed in NA-modified IPC has been well elucidated [23].

The crystallization behavior of two propylene–ethylene random copolymers was studied by Chrissafi and co-workers. Both copolymers have 7 wt.% ethylene units content. The combination of the preferable generation of β-crystals in one in contrast to another one which crystallizes in principle giving α-crystals, along with the random occurrence of the ethylene comonomer units, complicate the crystallization mechanism. In order to better understand the solidification processes in these complex systems, crystallization under isothermal and non-isothermal conditions, and also melting of the resulting crystalline structure was thoroughly investigated. The crystallization behavior of two random copolymers with different characteristics was studied with DSC. The strong dependence of the crystallization behavior on the crystalline structure was successfully demonstrated [24].

Xu and co-workers investigated the effect of nucleating agent mainly contained sodium benzoate on the crystalline morphologyof polypropylene (PP). From this paper it is understood that increasing nucleating agent has an effect on both high and low levels of the crystalline structure. The nucleating agent displayed a heterogeneous nucleation effect. The theory of heterogeneous nucleation of PP materials with a nucleating agent is not very mature, with much ongoing research. It is more stable for PP crystallization from a melt to form a gyroidal structure, with random coil molecules first transforming to this gyroidal structure as quickly as possibly [25].

Piorkowska and co-workers investigated nucleation of high pressure gamma form in isotactic polypropylene. They indicated that monoclinic alpha, hexagonal (trigonal) beta and orthorhombic gamma forms of Isotactic polypropylene (iPP). They defended that iPP crystallizes usually in the alpha or beta phase under atmospheric pressure; but crystallization of the gamma form is facilitated by high pressure. Owing to its unique structure with nonparallel chain alignment, the gamma form exhibits different mechanical properties than the alpha form. For this study, they used two alpha and beta form nucleating agents. Their results showed that α-NAs accelerated crystallization of iPP under high pressure in the gamma form whereas the beta-nucleating agent did not. They commented this effect as result of “seeds” of α-NA. The alpha-nucleating agents possibly acted by nucleating the alpha "seeds" and they mentioned about facilitating further crystallization of the gamma crystals relevant

this effect. In brief, this study showed that the possibility to nucleate the gamma form of iPP under high pressure [26].

3. EXPERIMENTAL

3.1 Materials

3.1.1 Recycled polypropylene

Oriented-Polypropylene (OPP) and diaper post-production wastes were reycled at Polipro Plastic Inc. using plastic recycler single screw extruder. The resultant plastic granules were used as main polymer matrix with the melt flow index of 15 g/10min (MFI; 230°C, 2.16 kg) and density is 0.92 g/cm^3. Besides, diaper wastes have 20g/10min MFI value, while OPP wastes have approximately 8g/10min MFI value

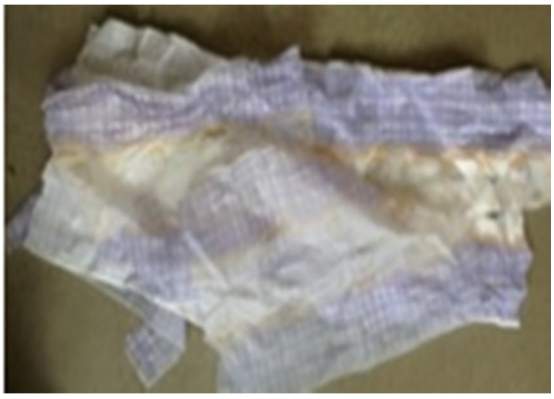

Figure 3.1 : Diaper waste

Figure 3.2 : OPP waste

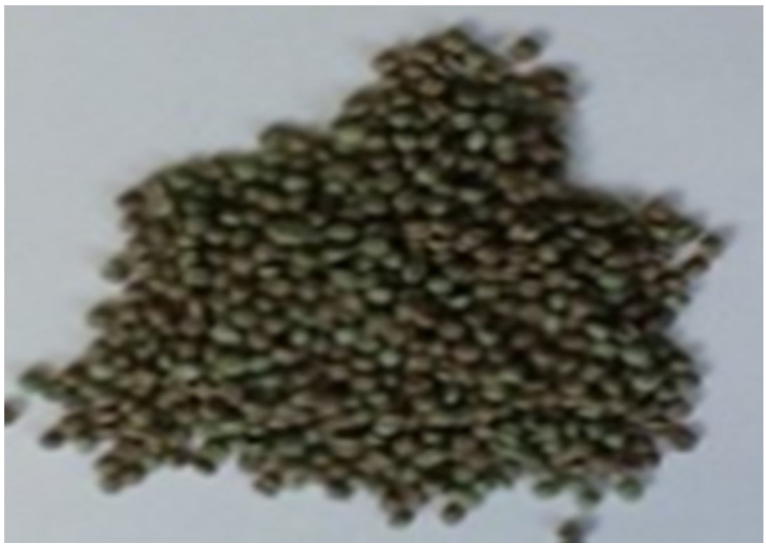

Figure 3.3 : Recycled plastic granules

3.1.2 Ethylene-propylene-diene-monomer (EPDM)

Ethylene-Propylene-Diene-Monomer (EPDM), which was used as a elastomeric additive, was supplied as granule by Mitsui Chemicals with trade name EPT. The different types of grades comprise of varying proportions of ethylene and diene. 3092 PM is placed non-oil extended grade with mooney viscosity 61ML(1+4)125 °C. It consists of %65 ethylene and %4,6 diene; has also low melt flow index and narrow molecular weight distribution [27].

Figure 3.4 : EPDM granules

3.1.3 Nucleating agents

Three types of nucleating agents were used. They have different chemical formulas.

3.1.3.1 ADK STAB NA-11UH

ADK STAB NA-11UH was supplied by Adeka. Its chemical name is Sodium 2,2'-Methylenebis-(4,6-di-tert-butylphenyl) phosphate. The Figure 3.5 shows the chemical structure of NA-11UH. [28]

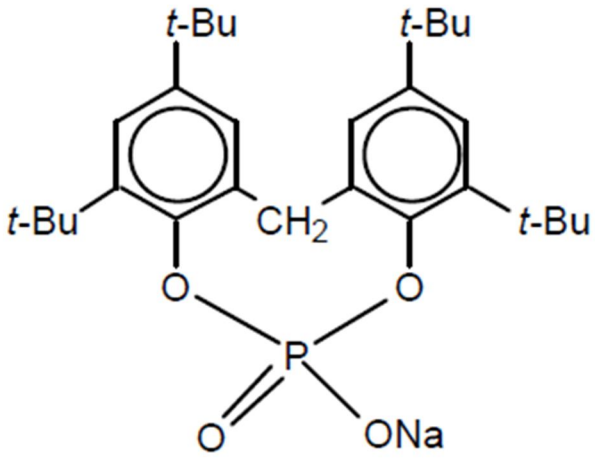

Figure 3.5 : Chemical formula of ADK STAB NA-11UH[29]

3.1.3.2 HYPERFORM

The other nucleating agents were supplied by Miliken with trade name Hyperform. HPN 68L is a powdered solid nucleating agent comprises a dicarboxylate Na-based compound and the Figure 3.6 shows the chemical structure of HPN 68L. [30, 31]

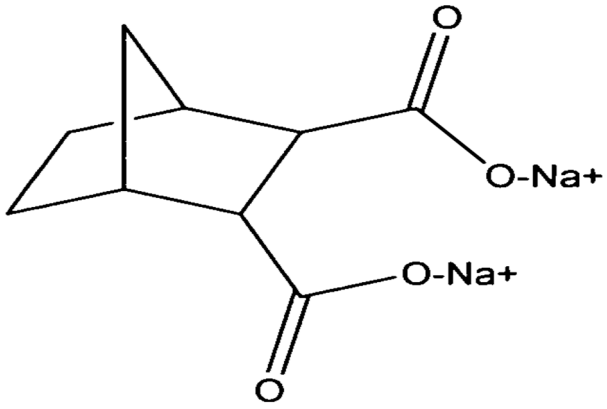

Figure 3.6 : Chemical formula of HPN 68L[30]

HPN 20E is a powdered solid nucleating agent contains “Ca HHPA” as shown in Figıre 3.7 [32,33].

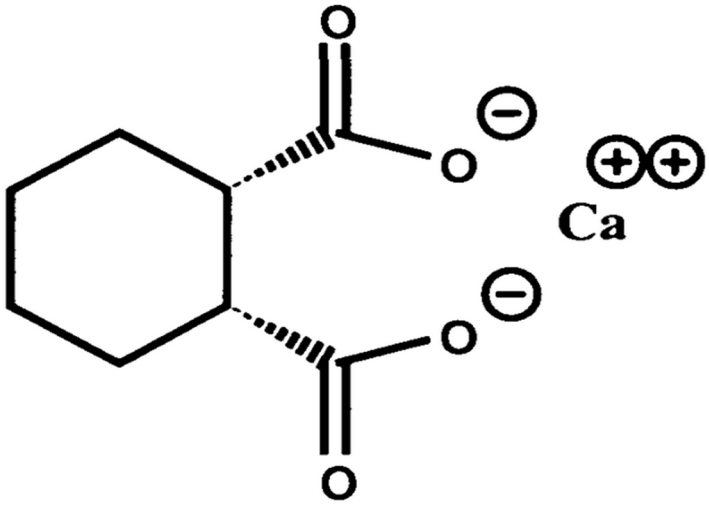

Figure 3.7 : Chemical formula of HPN 20E[34]

3.1.4 Antioxidant

Secondary antioxidant which was used as a processing stabilizer, was supplied by Ciba with trade name Irgafos 168. Its chemical name is Tris (2,4-di-tert-butylphenyl)phosphite and the Figure 3.8 shows the chemical structure of Irgafos 168 [35].

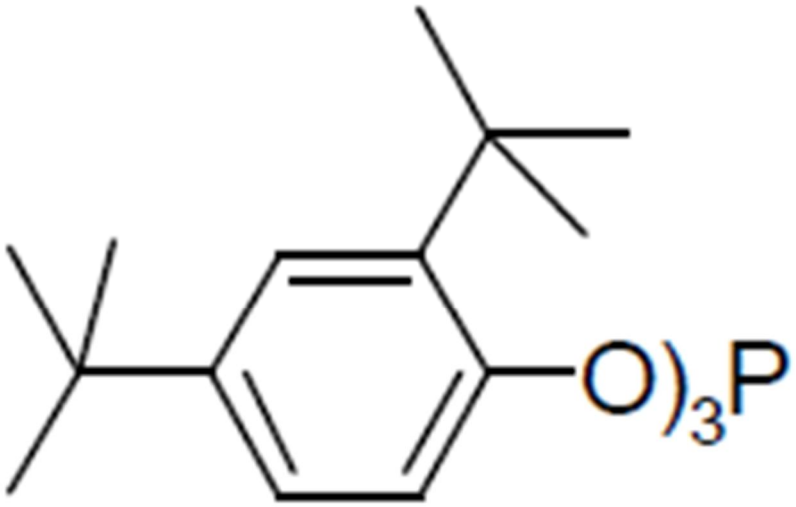

Figure 3.8 : Chemical formula of Irgafos 168[35]

3.2 Equipment

3.2.1 Twin-screw extruder

A intermeshing co-rotating twin-screw extruder was used; Polimer Teknik Poex T-27, with the screw diameter 27 mm and L/D ratio 48:1 to prepare compounds. The scheme of the extruder is given in Figure 3.9.

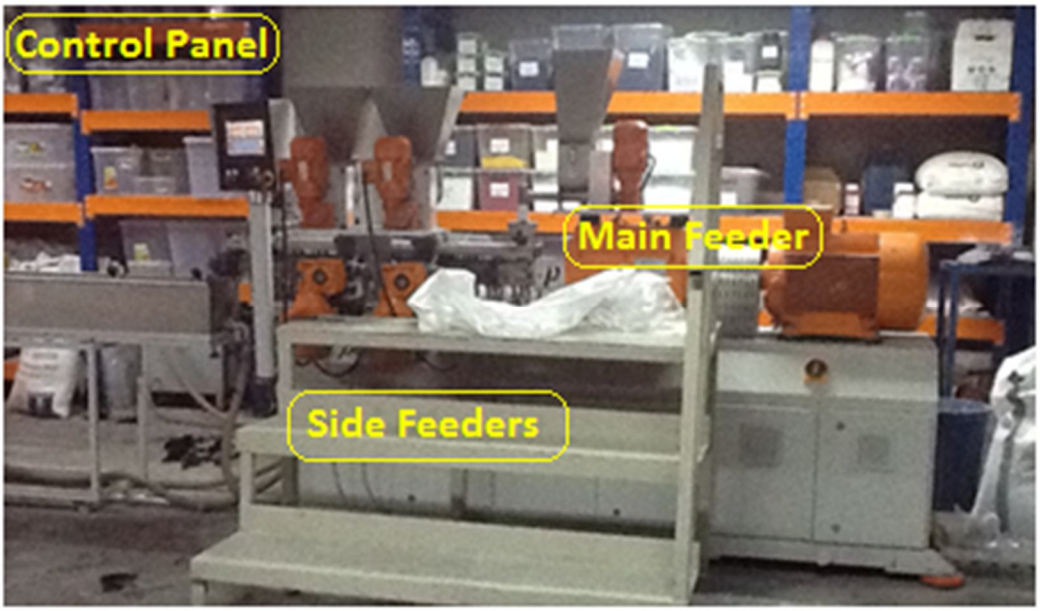

Figure 3.9 : Poex T-27 Twin-screw extruder

This extruder have one volumetric main feeder, two volumetric side feeders, degassing unit, water bath and fixed length pelletizer. Additional temperature and pressure measuring points are located in the closed barrel system. Electrical resistances and water cooling channels controlled by thermoregulator which are connected to each modular barrel zone to ensure play important role to control the set temperature. There are 13 temperature zones have ±1°C accuracy. Polymeric materials melt in the barrels by effect of heat and pressure. The gases occurred during compounding are removed and one degassing unit is connected to the vacuum pump by hoses at the 12^{th} barrel zone. Die takes place with a five-strand hole at the forward end of the extruder. Details of Poex T-27 extruder are given in Table 3.1.

Table 3.1 : Poex T-27 twin-screw extruder technical specifications[36]

Specification	Units	Poex T-27
Screw diameter	mm	27
Maximum screw speed	rpm	1200
L/D (shaft length/screw diameter)	-	48:1
Working length	mm	1296
Max. capacity	kg/h	5-100
Motor power	kW	30
Heating power	kW	12
Average water requirement	lt/min	30
Height	mm	1050
Total weight	kg	950
Max. pressure	bar	300
Vacuum pump	kW	0,75
Cooling unit (pump)	kW	0,5
Granulating motor	kW	2,2

The polymer melt can go out of the extruder. It can be cooled down into a water bath and obtained as spaghettis that are cut into small pieces called granules by the fixed length pelletizer or chopper. This system is also known as the classical way of spaghettis pelletizing. Figure 3.10 shows granulating unit.

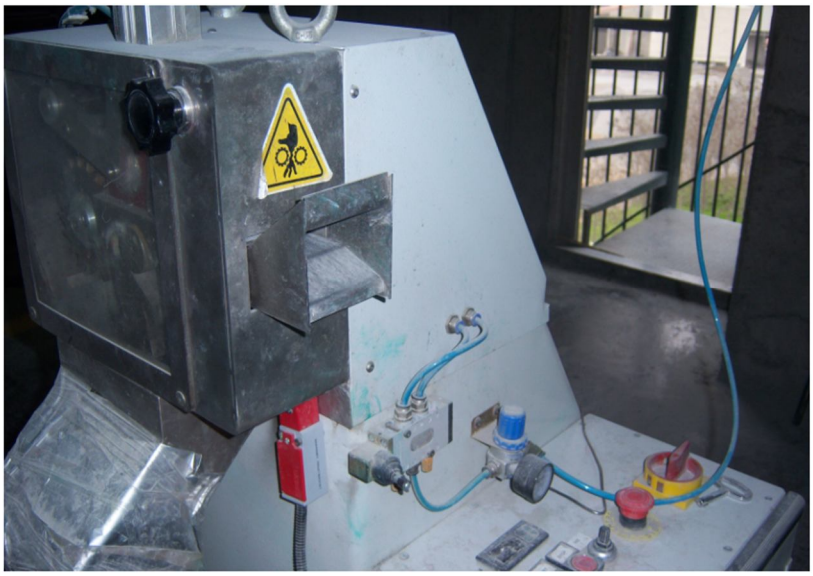

Figure 3.10 : Granulating Unit

3.2.1.1 Screw configuration

The used extruder was design to provide good melting and mixing with high shear and high residence time for compounding process. It has various types of configuration throughout the screw. The screw configuration used in this study contains 9 conveying blocks, 7 kneading blocks and solid conveying zone, plasticizing zone, melt conveying zone, homogenization zone, degassing zone, pressure built up zone. Raw material takes in by first conveying zone; then the material is plasticized, and the molten is obtained throughout following 3 kneading and 4 conveying zones. After that the molten is made homogenized by 3 kneading and 4 conveying blocks. Finally the gases occurred during compounding are removed by degassing zone.

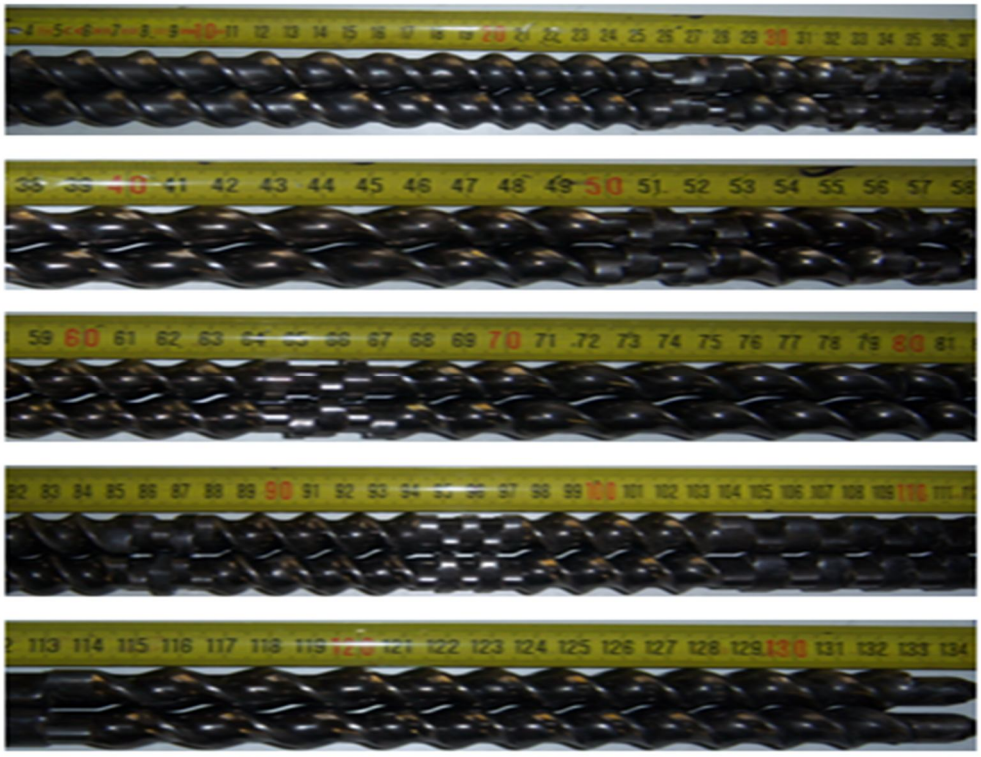

Figure 3.11 : Screw configuration of POEX T-27

3.2.2 Injection molding machine

Arburg injection machine was used to produce specimens according to ISO 527 standard as shown in Figure 3.12. Injection unit consists hopper, heat controlled barrels-cylinder, screw and motor. Technical specifications of the Arburg injection machine are given in the Table 3.2.

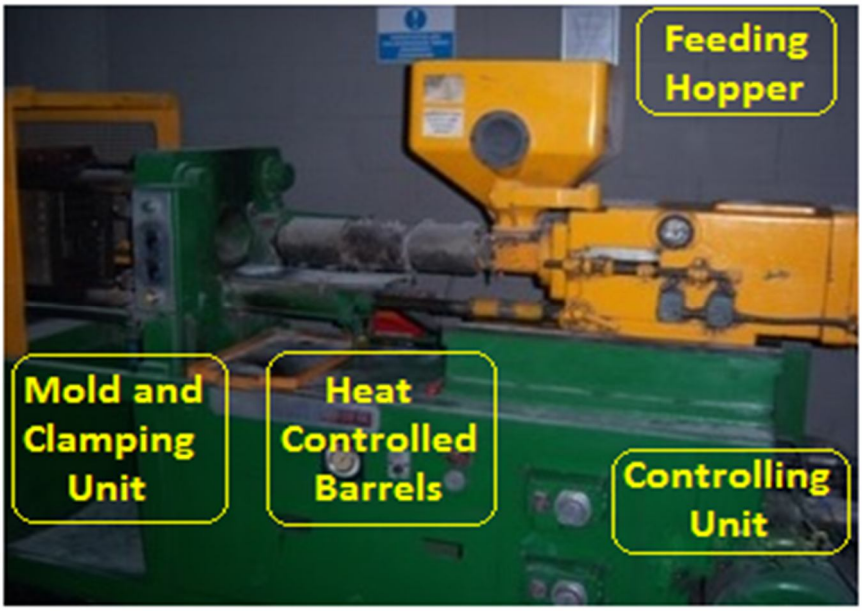

Figure 3.12 : Arburg injection molding machine

Table 3.2 : Arburg injection molding machine technical specifications

Specification	Unit	Arburg
Screw diameter	mm	27
Max. injection pressure	bar	950
Wax. Shot weight	g	78
Hydraulic motor power	W	1800
Max. clamping force	tonnes	20
Screw back pressure	bar	20

3.2.3 Density determination kit

The density of specimens was measured with Radwag Was 220/X density scale as shown in Figure 3.13.

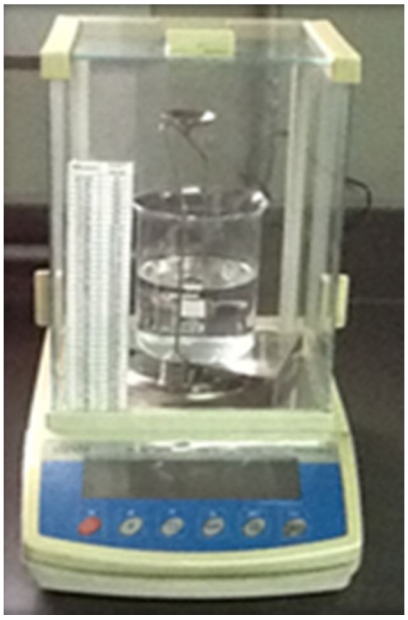

Figure 3.13 : Density determination kit

3.2.4 Melt flow index machine

Melt flow index (MFI) was measured by using Ceast Modular Base Model testing machine which could operate between 40 and 500 °C temperature range as shown in Figure 3.14.

Figure 3.14 : Melt flow index machine

3.2.5 X-ray diffractometer (XRD)

XRD analysis of samples was performed using Rigaku R-AXIS RAPID-S x-ray diffractometer as shown in Figure 3.15.

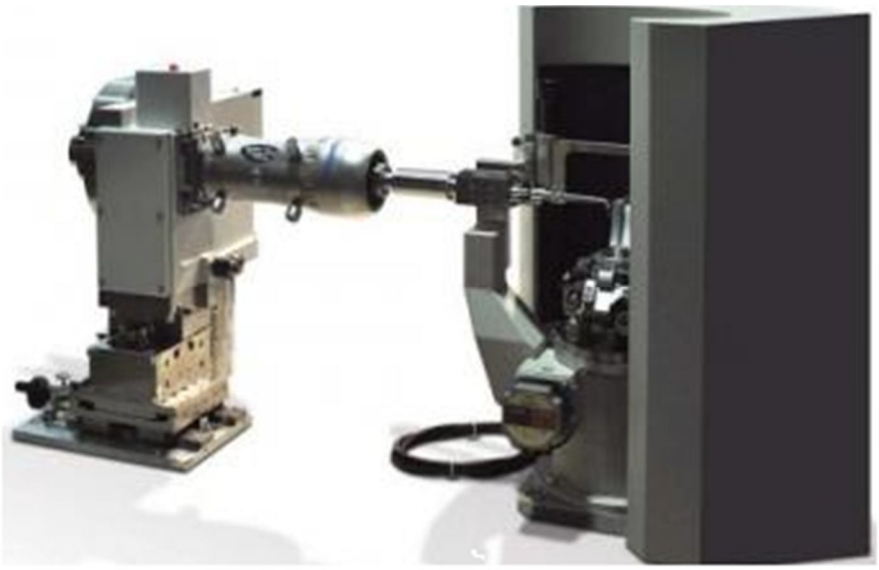

Figure 3.15 : X-ray diffraction instrument

3.2.6 Differerential scanning calorimeter (DSC)

Thermal analysis of the samples were done with TA Instruments Q20 Differential Scanning Calorimetry machine as shown in Figure 3.16 and technical specifications of the DSC are given in the Table 3.3.

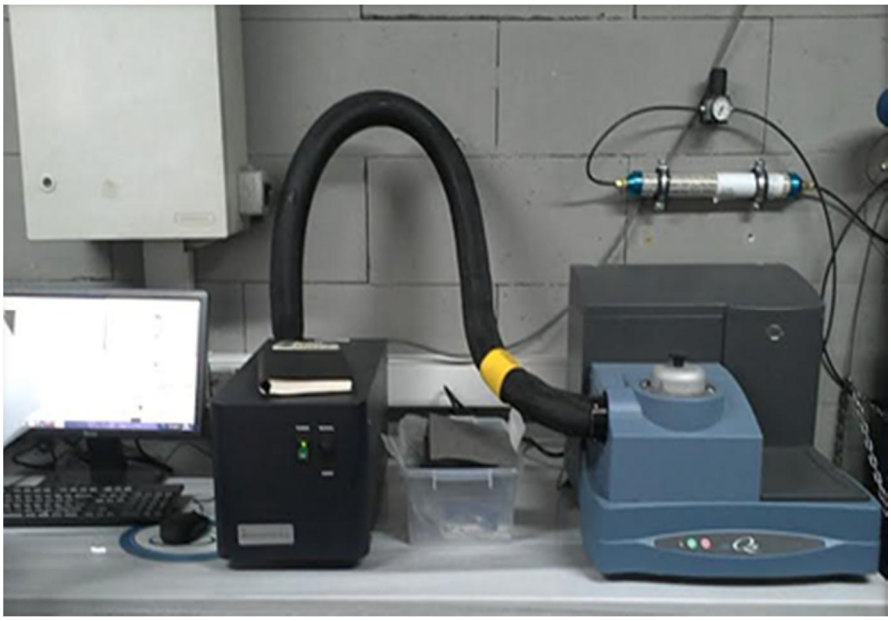

Figure 3.16 : Differential scanning calorimeter

Table 3.3 : TA Q20 DSC technical specifications[35]

Specification	TA Q20
Temperature range	Amb. to725 0C
With cooling accessories (RCS40)	-40 0C – 725 0C
Temperature accuracy	+/- 0,1 0C
Temperature precision	+/- 0,05 0C
Sensitivity	1,0 µW
Calorimetric precision (indium metal)	+/- 0,1 %
Indiyum height/width (mW/0C)	8

3.2.7 Polarizing Microscope (POM)

The morphologies of the samples were investigated by polarizing microscope Nikon, Eclipse LV100 as shown in Figure 3.17. In the study POM attached hot-stage which could operate between -80 °C and 400 °C temperature range was used.

Figure 3.17 : Polarizing microscope

3.2.8 Universal testing machine

Tensile properties of specimens were measured by using Lloyd LC universal tensile testing machine equipped with 5 kN load cell as load indicator and long stroke extensometer as extension indicator. Testing speed was set to 50 mm/min and gauge length (L_o) was set to 100 mm. Tensile testing machine is indicated in Figure 3.18

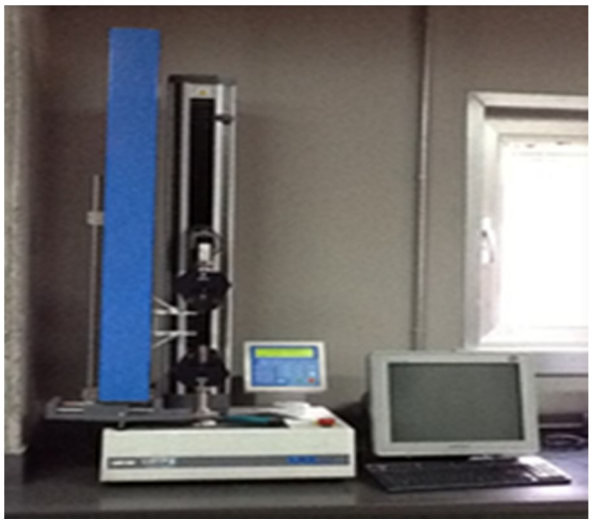

Figure 3.18 : Universal testing machine

3.2.9 Izod impact test machine

Izod impact strength of specimens was measured by using Ceast 9050 Izod impact machine which could operate between 0,5 and 25 Joule energy range as shown in Figure 3.19.

Figure 3.19 : Izod impact testing machine

3.2.10 Notching machine

2 mm-notch to specimens was opened for Izod impact test by using Ceast Manual notching machine as shown in Figure 3.20.

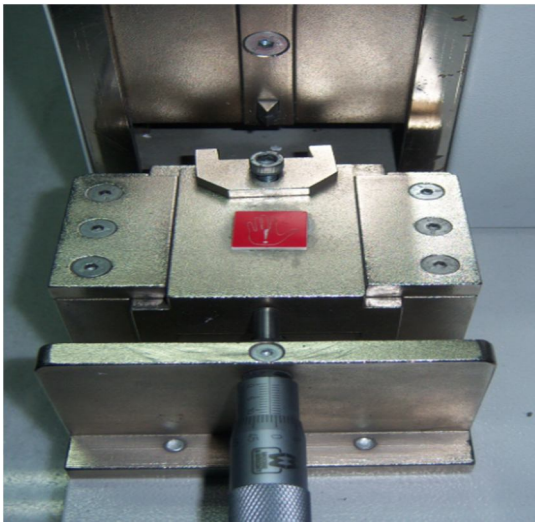

Figure 3.20 : Manual notching machine

3.2.11 Shore hardness tester

Shore-D hardness values were measured of the samples by using Shore-D hardness tester as shown in Figure 3.20.

Figure 3.21 : Shore Hardness Tester

3.3 Experimental Procedure

3.3.1 Compounding recipes

Formulations of compounds, containing recycled polypropylene (RPP) and mixtures of EPDM 3092 PM, nucleating agents (3 different grades; ADK STAB 11-UH, Hyperform 68L, Hyperform 20E) and antioxidant Irgafos 168, were processed using co-rotating twin-screw extruder.

Table 3.4 : Formulations of compounds (weight per centage)

SAMPLES	RPP	3092 PM	NA-11UH	HPN-68L	HPN-20E	Irgafos-168
RPP	100	-	-	-	-	-
RPP/5% EPDM	95	5	-	-	-	-
RPP/10% EPDM	90	10	-	-	-	-
RPP/NA-11UH	99.5	-	0.5	-	-	-
RPP/HPN 68L	99.5	-	-	0.5	-	-
RPP/HPN 20E	99.5	-	-	-	0.5	-
RPP/I-168	99.8	-	-	-	-	0.2
RPP/NA-11UH/I-168	99.3	-	0.5	-	-	0.2
RPP/HPN 68L/I-168	99.3	-	-	0.5	-	0.2
RPP/HPN 20E/I-168	99.3	-	-	-	-	0.2
RPP/5% 3092 PM/NA-11UH	94.5	5	0.5	-	0.5	-
RPP/5% 3092 PM/HPN 68L	94.5	5	-	0.5	-	-
RPP/5% 3092 PM/HPN 20E	94.5	5	-	-	0.5	-
RPP/10% 3092 PM/NA-11UH	89.5	10	0.5	-	-	-
RPP/10% 3092 PM/HPN 68L	89.5	10	-	0.5	-	-
RPP/10% 3092 PM/HPN 20E	89.5	10	-	-	0.5	-
RPP/5% 3092 PM/I-168	94.8	5	-	-	-	0.2
RPP/10% 3092 PM/I-168	89.8	10	-	-	-	0.2
RPP/5% 3092 PM/NA-11UH/I-168	94.3	5	0.5	-	-	0.2
RPP/5% 3092 PM/HPN 68L/I-168	94.3	5	-	0.5	-	0.2
RPP/5% 3092 PM/HPN 20E/I-168	94.3	5	-	-	0.5	0.2
RPP/10% 3092 PM/NA-11UH/I-168	89.3	10	0.5	-	-	0.2
RPP/10% 3092 PM/HPN 68L/I-168	89.3	10	-	0.5	-	0.2
RPP/10% 3092 PM/HPN 20E/I-168	89.3	10	-	-	0.5	0.2

During the preparation of every mixtures 3 phr black masterbatch was added in order to obtain better appearance of samples, and RPP-based compounds were prepared with varying the EPDM/Nucleating Agent/Antioxidant percentages according to formulation recipes given below in Table 3.4.

3.3.2 Compounding procedure and compounding process parameters

The extruder has 3 volumetric feeders:1 main feeder and 2 side feeders.The raw materials were firstly pre-mixed and mixtures were fed into extruder from inlet zone with using first feeder. The compounded materials were taken from the extruder via the holes of the die and cooled down in water bath and the pelletized by pelletizer. The properties of final product are affected process parameters that are known as temperature, screw speed etc. The temperature profile which was preferred for RPP was 70°C/170°C /170°C /175°C /185°C /185°C /190°C /190°C /195°C /195°C /205°C /210°C /210°C. Screw speed was determined as 500 rpm in order to disperse EPDM. All the process parameters were kept constant in order to prevent the negative effects.

3.3.3. Injection molding machine and process parameters

Injection molding is defined as a process where melt polymer forced into a mold cavity and cooled down in it by taking its shape. A plastic injection machine is mainly divided into three parts which are known as mold, clamping unit and injection unit. Polymeric materials are in the form of pellets and they are loaded into a hopper on top of the injection unit during the injection process. The pellets are fed into injection machine from feeding hopper and heated until they melt. When injection process begins, the speed controlled forward movement of screw forces molten plastic into mold cavity and then holds the force for a while to minimize the shrinkage of molded part. The mold is kept closed to cool down the melted plastic and give shape after finishing injection and holding pressure. Then, mold opens and molded-shaped parts are taken.

In this study, the barrel temperature and mold temperature were 210°C and 30°C, respectively. Melt flow index, tensile, Izod impact and hardness test specimens were produced with injection machine according to ISO 527 standard.

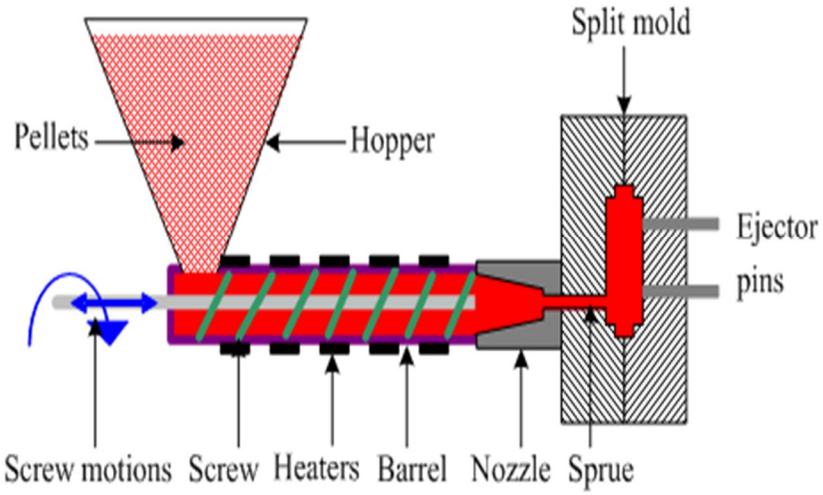

Figure 3.22 : Illustration of injection molding machine [36]

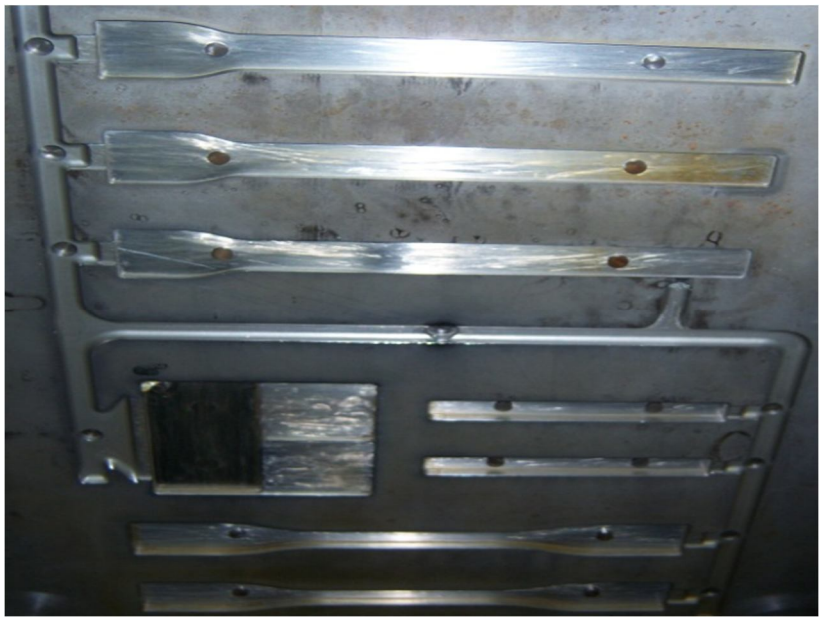

Figure 3.23 : The mold shape

3.4 Characterization

3.4.1 Structural, morphological and thermal properties

3.4.1.1 Measurement of density

The density of specimens was determined according to the procedure explained in ISO 1183. This method is worked according to "Archimedes Principles of Density

Measurement" and specific gravity. Specific gravity refers to the ratio of the density of a sample to the density of pure water.

The density of specimen was obtained according to the weight of the sample in air, weight in liquid and the density of the liquid.

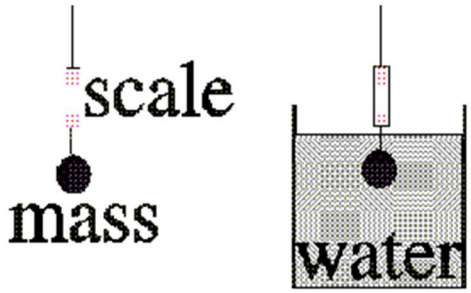

Figure 3.24 : Density determination of a solid[37]

3.4.1.2 Determination of melt flow index

The flow behavior of molten polymer is defined as an important factor affecting the processability of polymers. Melt flow index (MFI) or melt flow rate (MFR) is described by flow properties of the molten polymers and measured according to ISO 1133 test standard. [38]

Viscosity is a key determinant of the melting behavior of thermoplastics. A high temperature both increases the mobility of the polymer chains and breaks chemical bonds to create smaller fragments; thus viscosity is a function of both molecular weight and temperature. Polymers having high viscosity value in other words high molecular weight shows low melt flow index. Breaking of polymers chain causes increases on melt flow index. However, this situation limits the mechanical properties of polymers. This situation is bigger problem for especially recycled plastics. Thermal and oxidative degradation occuring in their structure before recycling process, and exposing to temperature and shear stresses causes much higher losses in terms of mechanical properties. This situation causes to brittleness of the material, deterioration of the mechanical and surface properties; also decreasing of stability and limiting the end production applications.

3.4.1.3 X-ray diffraction (XRD) analysis

XRD measurements were carried out for structural analyses of samples. RPP and ternary mixtures were analyzed in order to observed differences in structures under radiation.The analyses were performed at a voltage of 45 KV, 40 mA with CuK_{α}

radiation (wavelength = 1.5405 °A = 0.15405 nm) by 2θ at a scan rate of 2 °/min in the interval from 10 to 45.

The results of analysis was calculated by using "Bragg's Law" equation as shown in Figure. n is an integer determined by the order given, λ is the wavelength of x-rays, and moving electrons, protons and neutrons, d is the spacing between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes.

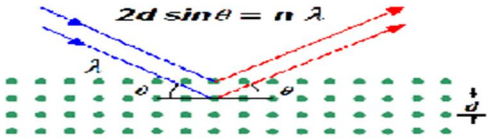

Figure 3.25 : Bragg's Law[39]

3.4.1.4 Differential scanning calorimetry analysis

The analysis were done according to ISO 11357-1 for all blends between 25ºC and 300ºC at 10ºC/min heating rate under nitrogen atmosphere. Melting temperatures (Tm), crystallization temperatures (Tg), the entalphy of melting and the enthalpy of crystallization values of the compounds were obtained using a differential scanning calorimeter (DSC).

3.4.1.5 Polarizing microscopy (POM) analysis

Polarizing microscope attached hot-stage was used in order to observe spherulite growth kinetics with on-line recording. Heating and cooling limits were determined taking DSC diagrams as reference. Firstly the samples were heated from room temperature to 250 °C, then they were kept at constant temperature (250 ºC) for ten minutes. After that, the samples was cooled from 250 ºC to 110 ºC with 1ºC/min cooling rate by using liquid nitrogen. The video recording was started with 50 µm zoom rate from 140 °C to 110 °C. Low cooling rate as 1ºC/min was selected for better observation of crystallization behaviour and spherulite growth.

3.4.2 Mechanical properties

3.4.2.1 Determination of tensile properties

Tensile properties of polymeric compounds were investigated by using tensile test specimens described as test specimens 'Type One' according to ISO 527. The test was carried out at standard conditions at 23 ± 2°C.

Tensile properties were measured as follow:

- Tensile stress or yield stress is indicated as σ_y (tensile load per unit area of original cross section within the narrow parallel portion). Tensile stress expressed in Newton per square millimeter (N/mm^2) is the first point on the load / extension curve at which an increase occurs without an increase in load.
- Tensile strain or percentage elongation at yield is indicated as ε_y. Tensile strain is the percentage elongation corresponding to tensile point.
- Elastic modulus or Young modulus is calculated from the slope of the line in this region where stress is proportional to strain.

3.4.2.2 Determination of Izod impact strength

Izod impact strength of specimens was determined according to ISO 180/1A standard. The thickness and width of the samples were measured by screw micrometer reading. Then, 2 mm-notch was opened by using manual notching machine. The specimen was placed into test machine grips in such a way that the notched surface was faced to the impact point. The pendulum was then released and the impact energy was recorded after making correction for frictional losses. The Izod impact strength, in kilojoules per square meter (KJ/m^2), as calculated as follow:

$$\text{Izod Impact Strength} = A_k / (X \times Y_k) \times 10^3$$

where A_k is the impact energy, in joules, absorbed by the test specimens and it is corrected for frictional losses. X is the thickness, in millimeters, of specimen. Y_k is the difference of width and notch depth, in millimeters.

3.4.2.3 Determination of Shore hardness value

Shore-D hardness value of the samples was measured according to ISO 868 standard. Shore hardness is tested with an instrument called Durometer. Durometer utilizes an

indenter loaded by a calibrated spring. The measured hardness is determined by the penetration depth of the indenter under the load. Since the samples are plastics, Shore-D type scale was used.

4. RESULTS AND DISCUSSION

In this study, 3 phr black masterbatch added RPP compounds with EPDM/Nucleating agent/Antioxidant mono, binary and ternary mixtures were prepared as weight percent according to procedure given in the section 3.3.2. EPDM was used in mixtures with two compositions as 5-10%; 3 different grades of nucleated agent were used in mixtures with 0.5% ratio and antioxidant was used in mixtures with 0.2 % ratio for preparing 24 mixtures. These produced were molded as test specimen and the samples were characterized as described in Section 3.4. All tests were repeated five times and standard deviations of the results were calculated.

4.1. Test Results of Structural, Morphological and Thermal Properties

Structural, morphological and thermal properties of polypropylene compounds were determined by using density, MFI, XRD, DSC and POM analyses.

4.1.1 Measurement of density

Measurement of density was done as defined in section 3.4.1.1. Test results were given in Table 4.1. Besides, graphical displays of test results for mono, binary and ternary mixtures were given Figures 4.1, 4.2, 4.3, respectively.

Test results showed that density values of compounds are nearly the same due to using additives such as EPDM, nucleating agents and/or antioxidant are not fillers, then densities of the samples are not affected

Table 4.1 : Test results of density measurements of the samples

SAMPLES	Density (g/cm3)
RPP	0.92 ± 0.01
RPP/5% EPDM	0.92 ± 0.02
RPP/10% EPDM	0.93 ± 0.01
RPP/NA-11UH	0.94 ± 0.01
RPP/HPN 68L	0.94 ± 0.01
RPP/HPN 20E	0.94 ± 0.01
RPP/I-168	0.94 ± 0.02
RPP/NA-11UH/I-168	0.93 ± 0.01
RPP/HPN 68L/I-168	0.94 ± 0.01
RPP/HPN 20E/I-168	0.93 ± 0.02
RPP/5% 3092 PM/NA-11UH	0.94 ± 0.02
RPP/5% 3092 PM/HPN 68L	0.93 ± 0.02
RPP/5% 3092 PM/HPN 20E	0.93 ± 0.01
RPP/10% 3092 PM/NA-11UH	0.94 ± 0.01
RPP/10% 3092 PM/HPN 68L	0.94 ± 0.01
RPP/10% 3092 PM/HPN 20E	0.93 ± 0.02
RPP/5% 3092 PM/I-168	0.94 ± 0.01
RPP/10% 3092 PM/I-168	0.93 ± 0.01
RPP/5% 3092 PM/NA-11UH/I-168	0.94 ± 0.01
RPP/5% 3092 PM/HPN 68L/I-168	0.93 ± 0.02
RPP/5% 3092 PM/HPN 20E/I-168	0.94 ± 0.01
RPP/10% 3092 PM/NA-11UH/I-168	0.94 ± 0.01
RPP/10% 3092 PM/HPN 68L/I-168	0.93 ± 0.01
RPP/10% 3092 PM/HPN 20E/I-168	0.94 ± 0.02

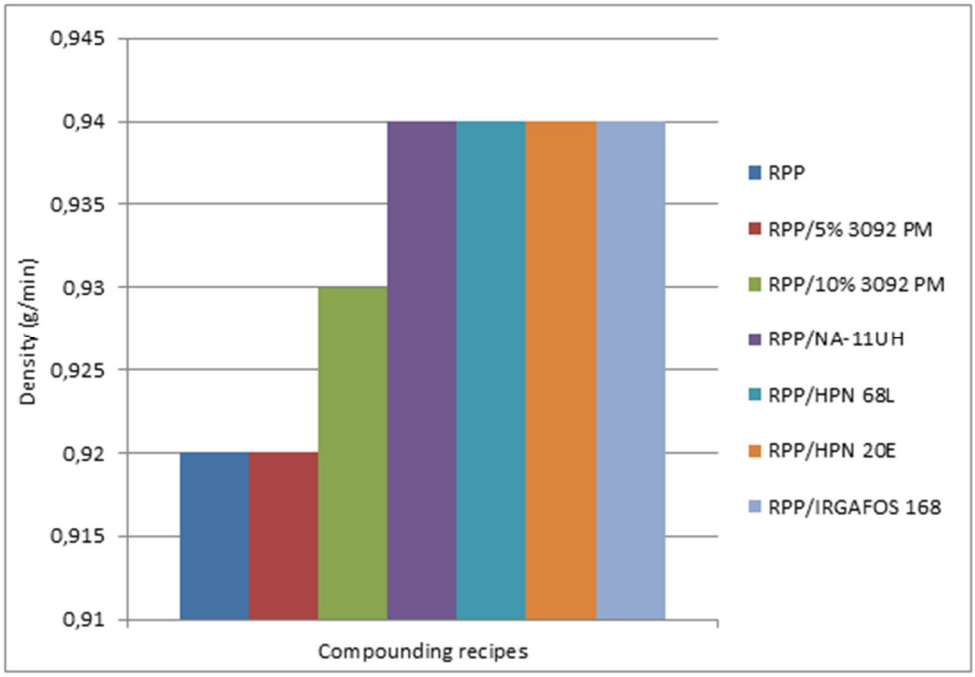

Figure 4.1 : Density values of mono mixtures

Recycled Polypropylene has a density of 0.92 g/cm^3 and compounds containing EPDM/N.A/A.O have approximately 0.93 or 0.94 g/cm^3, so that the results indicated that there were no significant differences for compunds based-RPP in terms of density values.

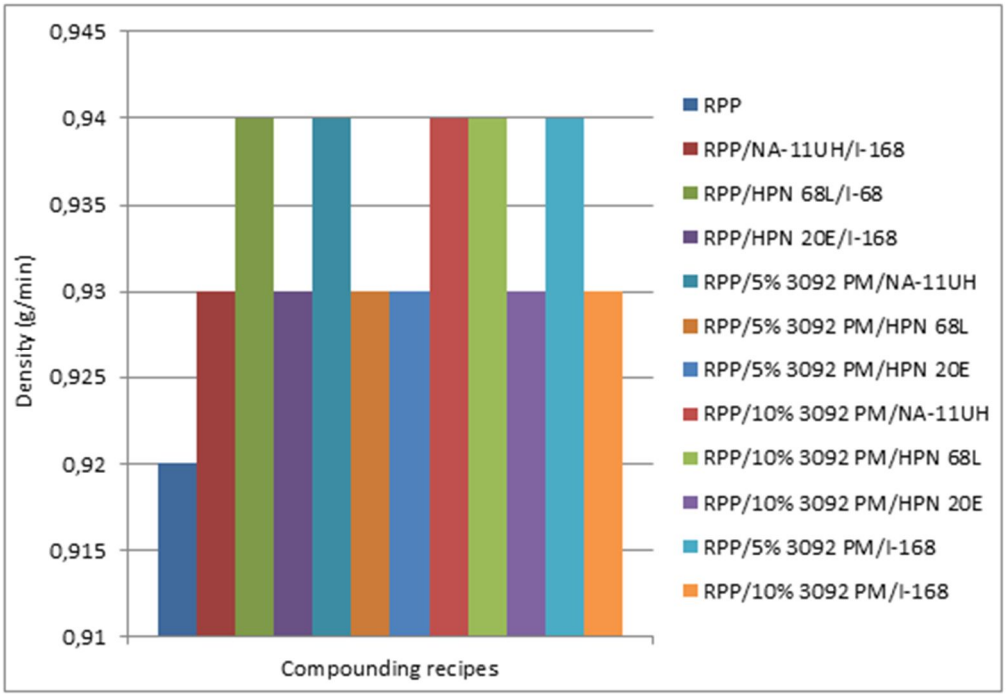

Figure 4.2 : Density values of binary mixtures

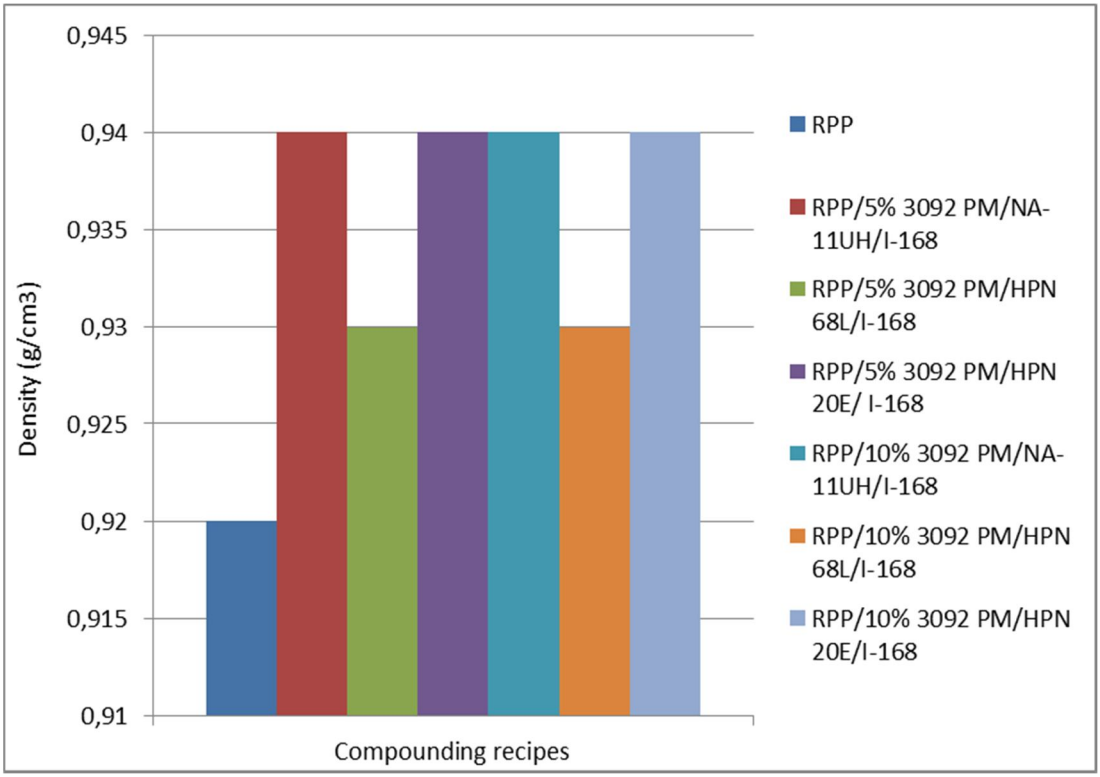

Figure 4.3 : Density values of ternary mixtures

4.1.2 Determination of melt flow index

Melt flow index (MFI) test was done as described in section 3.4.1.2. The test temperature and weight were set to 230°C and 2.16 kg. The densities of samples were used for measurement. Test results are given in Table 4.2. Besides, graphical displays of test results for mono, binary and ternary mixtures were given Figures 4.4, 4.5, 4.6, respectively.

MFI test results indicated a decrease with increasing loading level of EPDM. Recycled polypropylene has MFI of 15 g/10 min. The loading of 5% EPDM decreased MFI to 9.1 g/min, and the loading of 10% EPDM decreased MFI up to 8.4 g/10 min as shown in Figure 4.4. However, the types of nucleating agents causes approximately 0.2 g/10 min decrease compared to RPP, the antioxidant Irgafos 168 causes 0.3 g/10 min decrease; so these deviations can be neglected.

Table 4.2 : Test results of melt flow index measurements of the samples

SAMPLES	MFI (g/10min)
RPP	15 ± 0.8
RPP/5% EPDM	9.1 ± 0.5
RPP/10% EPDM	8.4 ± 0.6
RPP/NA-11UH	14.7 ± 0.9
RPP/HPN 68L	14.8 ± 0.5
RPP/HPN 20E	14.7 ± 0.9
RPP/I-168	14.7 ± 0.8
RPP/NA-11UH/I-168	14.9 ± 0.7
RPP/HPN 68L/I-168	14.8 ± 0.3
RPP/HPN 20E/I-168	14.9 ± 0.2
RPP/5% 3092 PM/NA-11UH	9.3 ± 0.6
RPP/5% 3092 PM/HPN 68L	9.5 ± 0.4
RPP/5% 3092 PM/HPN 20E	9.5 ± 0.7
RPP/10% 3092 PM/NA-11UH	8.2 ± 0.7
RPP/10% 3092 PM/HPN 68L	8.6 ± 0.9
RPP/10% 3092 PM/HPN 20E	8.4 ± 0.7
RPP/5% 3092 PM/I-168	9.6 ± 0.6
RPP/10% 3092 PM/I-168	8.1 ± 0.5
RPP/5% 3092 PM/NA-11UH/I-168	9.2 ± 0.9
RPP/5% 3092 PM/HPN 68L/I-168	9.3 ± 0.8
RPP/5% 3092 PM/HPN 20E/I-168	9.4 ± 0.5
RPP/10% 3092 PM/NA-11UH/I-168	8.1 ± 0.8
RPP/10% 3092 PM/HPN 68L/I-168	8.5 ± 0.3
RPP/10% 3092 PM/HPN 20E/I-168	8.2 ± 0.4

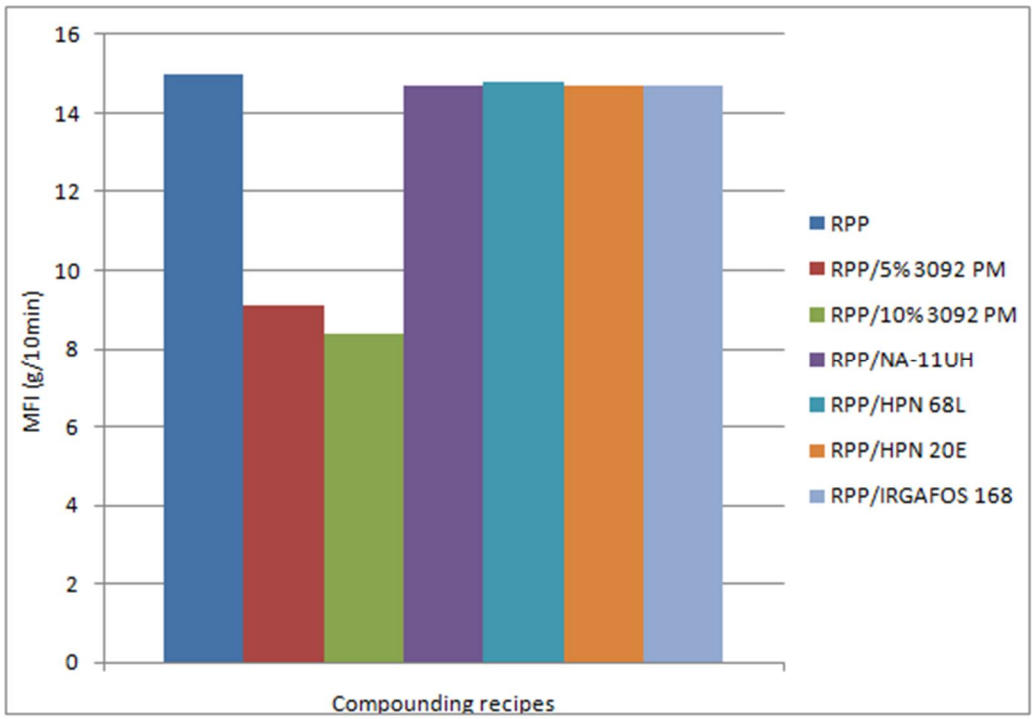

Figure 4.4 : MFI values of mono mixtures

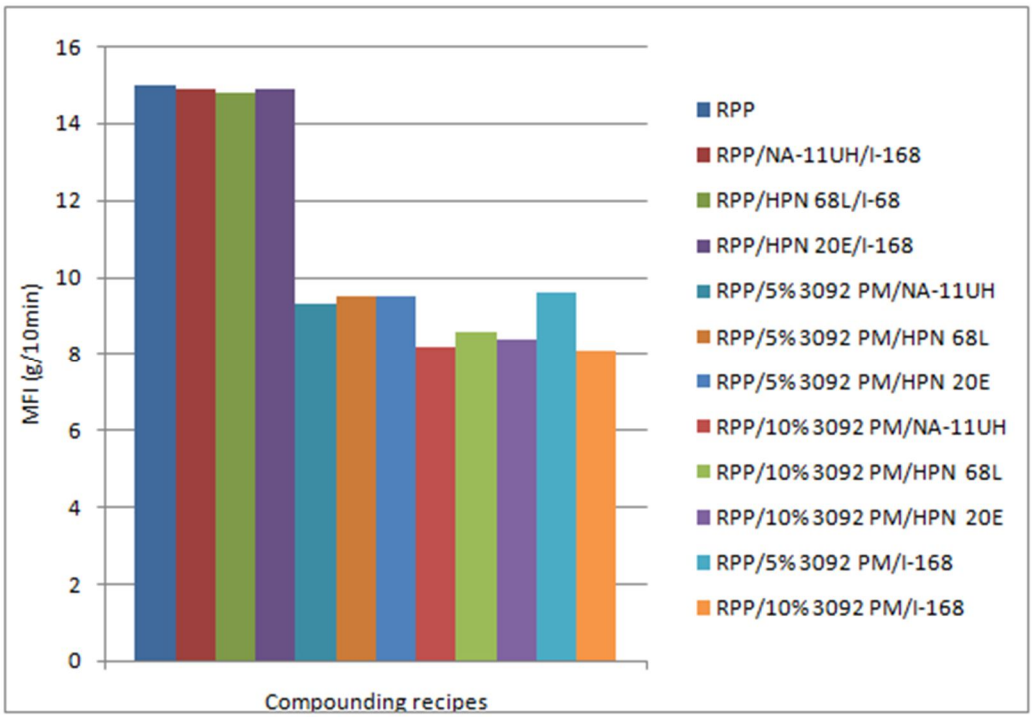

Figure 4.5 : MFI values of binary mixtures

Besides, the MFI values of ternary mixtures approximately obtained as 9.3 g/10 min for having 5% EPDM loading level; and moreover 8.2 g/10 min for having 10% EPDM loading level as shown in Figure 4.6.

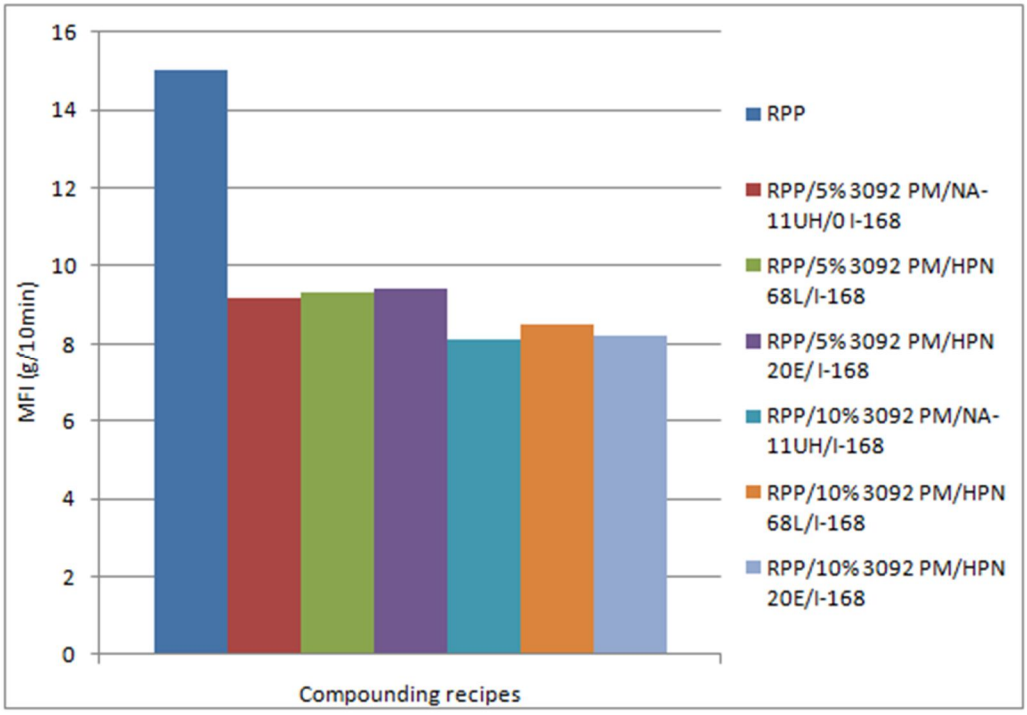

Figure 4.6 : MFI values of ternary mixtures

4.1.3 X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) analysis was done as described in section 3.4.1.3. Test results are given in Tables 4.3, 4.4, 4.5, 4.6. Besides, graphical displays of test results for mono and ternary mixtures were given in Appendix A.1.

Table 4.3 : Test results of X-ray diffraction analysis of the samples for first peak

SAMPLES	2θ(°)	Intensity	d
RPP	13.8	1933	6.42
RPP/5% 3092 PM/NA-11UH/I-168	13.8	1938	6.42
RPP/5% 3092 PM/HPN 68L/I-168	14.1	3920	6.28
RPP/5% 3092 PM/HPN 20E/I-168	14.1	2946	6.28
RPP/10% 3092 PM/NA-11UH/I-168	13.9	3653	6.36
RPP/10% 3092 PM/HPN 68L/I-168	14	4911	6.33
RPP/10% 3092 PM/HPN 20E/I-168	14	1635	6.33

Table 4.4 : Test results of X-ray diffraction analysis of the samples for second peak

SAMPLES	2θ(°)	Intensity	d
RPP	16.6	3118	5.34
RPP/5% 3092 PM/NA-11UH/I-168	16.6	3624	5.34
RPP/5% 3092 PM/HPN 68L/I-168	16.9	4844	5.24
RPP/5% 3092 PM/HPN 20E/I-168	16.9	7728	5.24
RPP/10% 3092 PM/NA-11UH/I-168	16.7	5384	5.304
RPP/10% 3092 PM/HPN 68L/I-168	16.8	5330	5.28
RPP/10% 3092 PM/HPN 20E/I-168	16.8	7588	5.28

Table 4.5 : Test results of X-ray diffraction analysis of the samples for third peak

SAMPLES	2θ(°)	Intensity	d
RPP	18.2	1438	4.87
RPP/5% 3092 PM/NA-11UH/I-168	18.2	1488	4.87
RPP/5% 3092 PM/HPN 68L/I-168	18.5	2524	4.79
RPP/5% 3092 PM/HPN 20E/I-168	18.5	1966	4.79
RPP/10% 3092 PM/NA-11UH/I-168	18.4	2316	4.82
RPP/10% 3092 PM/HPN 68L/I-168	18.4	2667	4.81
RPP/10% 3092 PM/HPN 20E/I-168	18.4	1476	4.82

Table 4.6 : Test results of X-ray diffraction analysis of the samples for fourth peak

SAMPLES	2θ(°)	Intensity	d
RPP	21.1	1543	4.19
RPP/5% 3092 PM/NA-11UH/I-168	21.2	1494	4.19
RPP/5% 3092 PM/HPN 68L/I-168	21.5	2107	4.13
RPP/5% 3092 PM/HPN 20E/I-168	21.5	1673	4.13
RPP/10% 3092 PM/NA-11UH/I-168	21.2	1954	4.19
RPP/10% 3092 PM/HPN 68L/I-168	21.4	2094	4.15
RPP/10% 3092 PM/HPN 20E/I-168	21.4	1608	4.15

The effect of nucleating agent on crystallization behaviour was determined based on XRD results. Nucleating agent changed "θ" angles and intesities of recycled PP as shown in shifted graphic Figure 4.7 α-NA additives caused higher θ and intensity value as indicator of monoclinic structure.

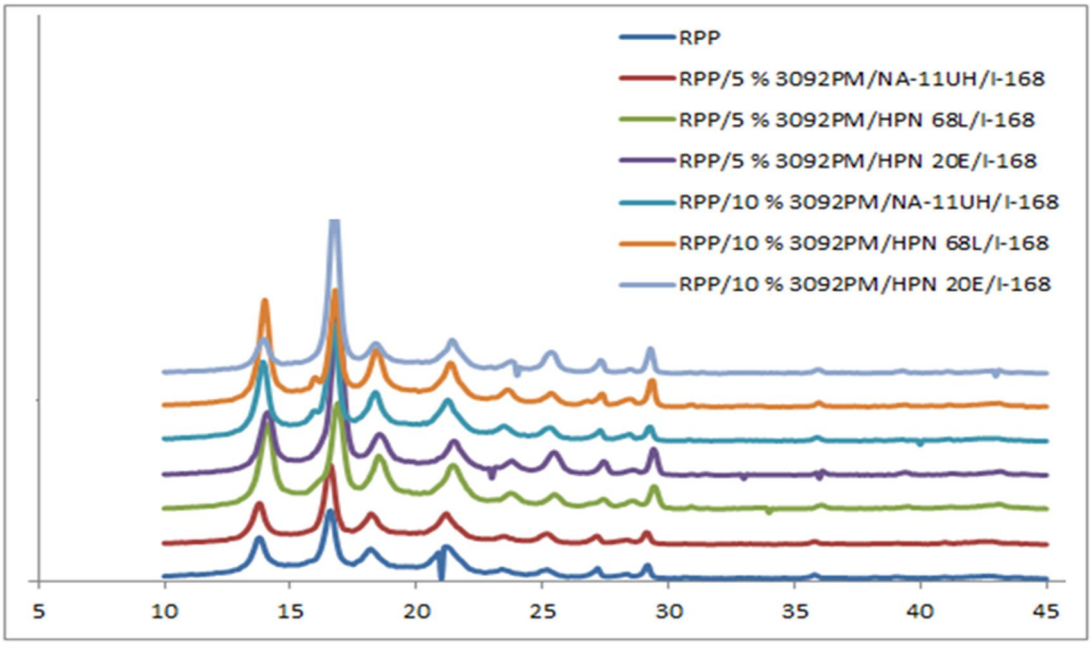

Figure 4.7 : Comparison of XRD results

4.1.4 Differential scanning calorimetry (DSC) analysis

Differential scanning calorimetry test was done according to the procedure explained in section 3.4.1.4. Differential scanning calorimetry test results are given in Table 4.7. Besides, graphical displays of test results for mono, binary and ternary mixtures were given in Appendix A.2.

Comparative diagrams were showed for crystallization peaks in Figures 4.8, 4.9, 4.10, 4.11, 4.12, 4.13; for melting peaks in Figures 4.14, 4.15, 4.16, 4.17, 4.18, 4.19. DSC diagrams showed that recycled PP contains approximately 5% polyethylene as shown in all comparative diagrams. The effect of α- nucleating agents was observed clearly in terms of crystallization behaviour in diagrams.

Table 4.7 : Test results of DSC measurements of the samples

SAMPLES	Tc (°C)	Tm (°C)	ΔHc (J/g)	ΔHm (J/g)
RPP	121	163	55	34
RPP/5% EPDM	122	163	62	54
RPP/10% EPDM	121	166	63	52
RPP/NA-11UH	130	163	76	62
RPP/HPN 68L	129	165	62	51
RPP/HPN 20E	130	165	53	44
RPP/I-168	121	166	55	47
RPP/NA-11UH/I-168	131	164	73	60
RPP/HPN 68L/I-168	131	163	68	57
RPP/HPN 20E/I-168	126	165	59	54
RPP/5% 3092 PM/NA-11UH	131	164	72	60
RPP/5% 3092 PM/HPN 68L	131	163	57	50
RPP/5% 3092 PM/HPN 20E	126	164	64	56
RPP/10% 3092 PM/NA-11UH	131	166	65	53
RPP/10% 3092 PM/HPN 68L	132	162	60	50
RPP/10% 3092 PM/HPN 20E	127	165	63	56
RPP/5% 3092 PM/I-168	122	164	61	55
RPP/10% 3092 PM/I-168	122	163	62	54
RPP/5% 3092 PM/NA-11UH/I-168	130	164	66	57
RPP/5% 3092 PM/HPN 68L/I-168	132	165	67	52
RPP/5% 3092 PM/HPN 20E/I-168	125	164	55	50
RPP/10% 3092 PM/NA-11UH/I-168	130	164	56	50
RPP/10% 3092 PM/HPN 68L/I-168	132	165	46	39
RPP/10% 3092 PM/HPN 20E/I-168	127	164	58	52

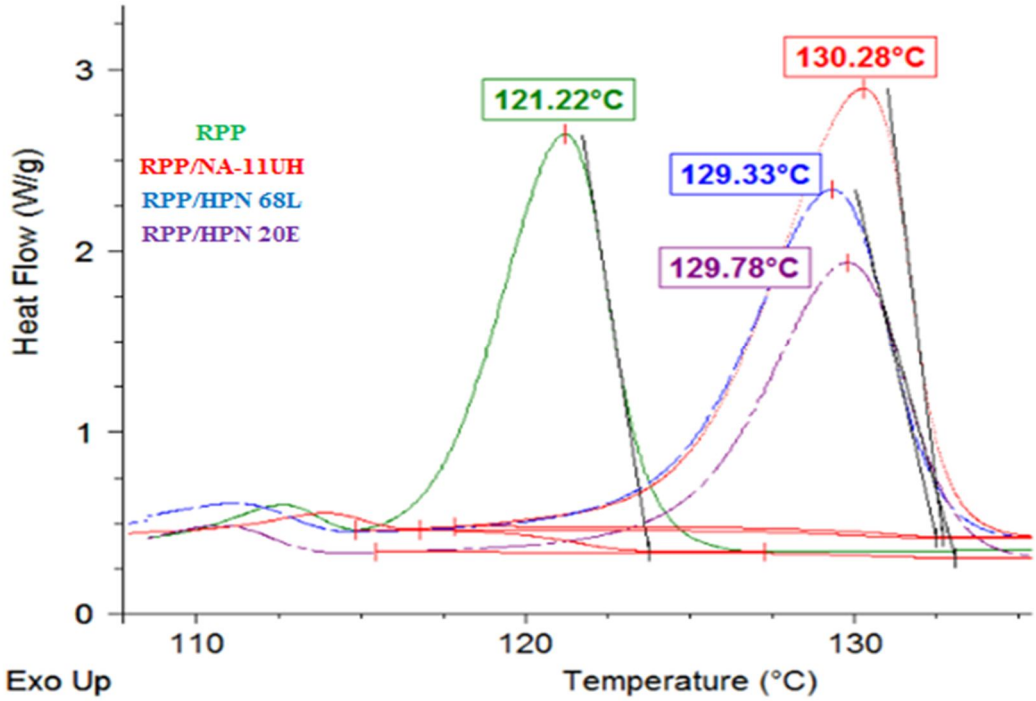

Figure 4.8 : Crystallization peaks of mono mixtures

From DSC results; it is observed that nucleating agents increased crystallization temperature and nucleated samples started to crystallize earlier according to recycled PP. Mono mixtures added α-NAs had higher crystallization temperatures compared to RPP as shown in Figure 4.8. RPP started to crystallize at 121.22 °C while mono mixtures added α-NAs started to crystallize at higher than 129 °C.

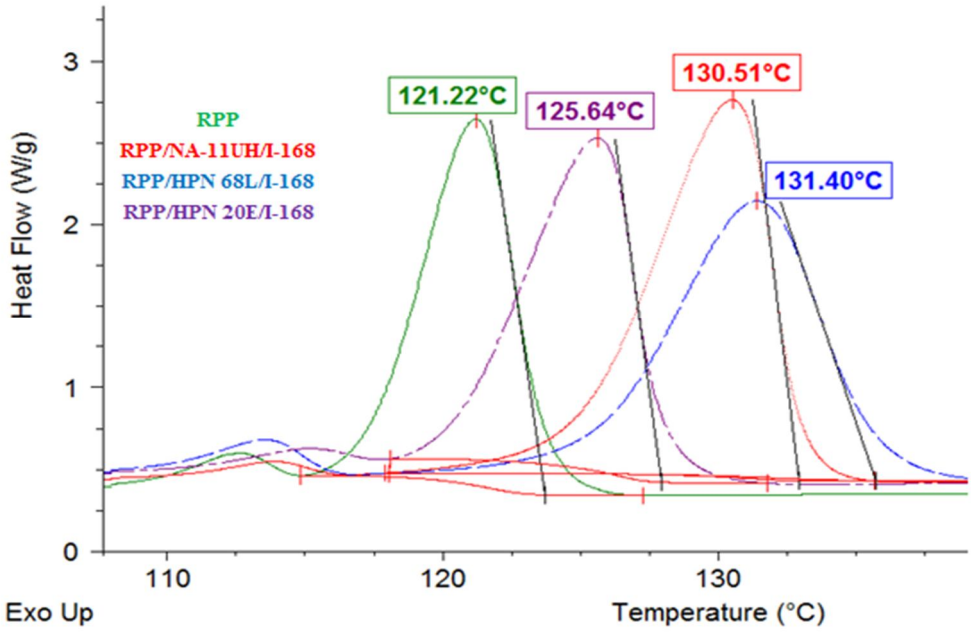

Figure 4.9 : Crystallization peaks of binary mixtures

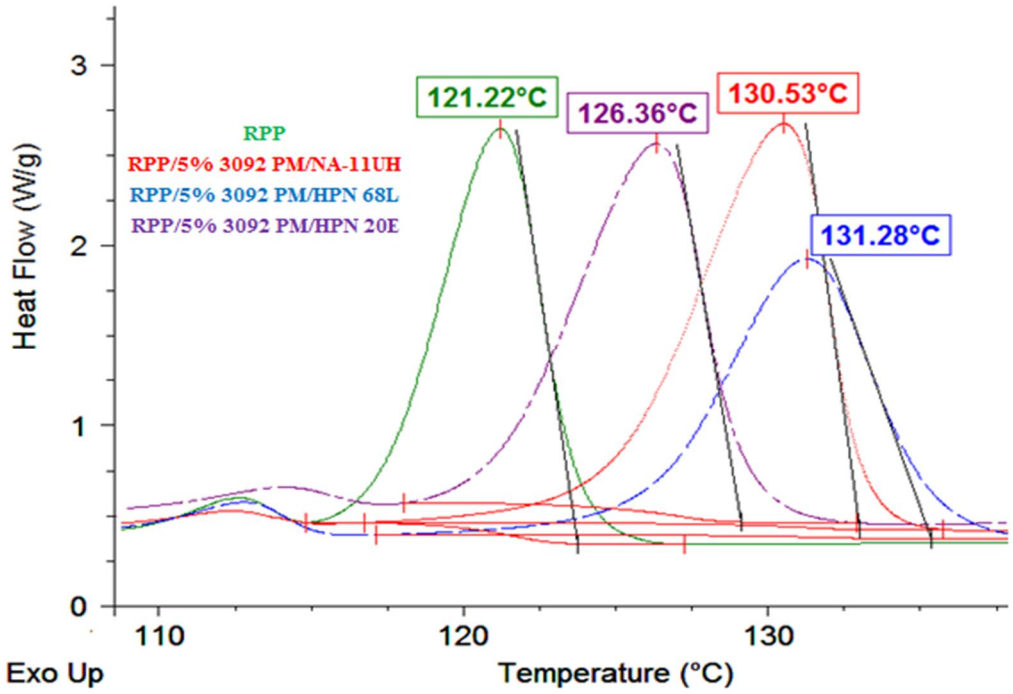

Figure 4.10 : Crystallization peaks of binary mixtures (with 5% EPDM)

The same α-NA effect seen in mono mixtures was observed in binary and ternary mixtures, nucleated samples started to crystallize earlier according to recycled PP.

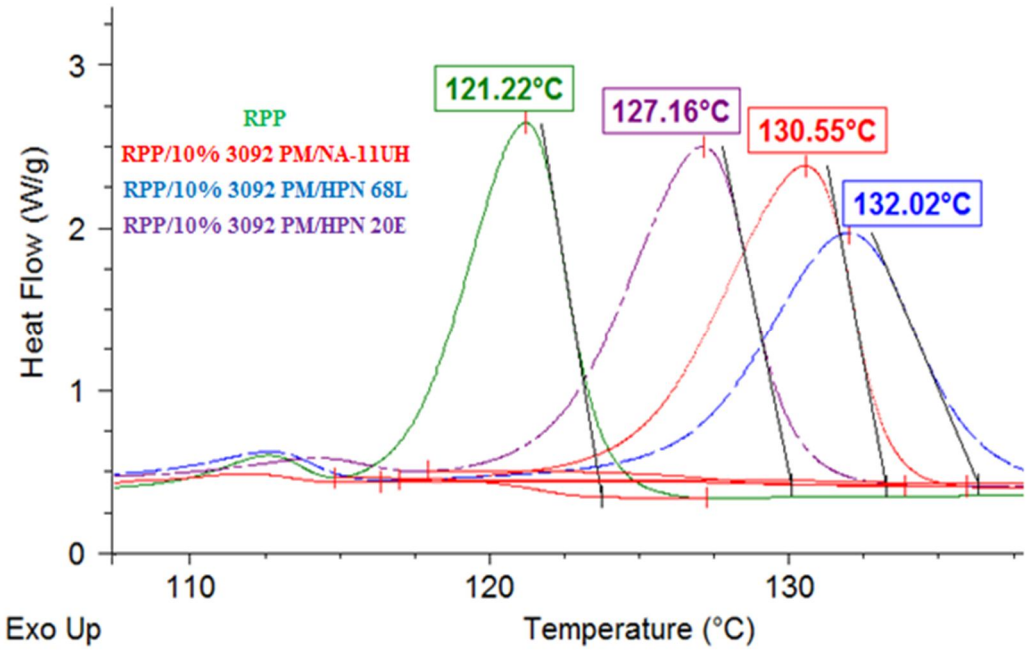

Figure 4.11 : Crystallization peaks of binary mixtures (with 10% EPDM)

The types of nucleating agents showed different effects on crystallization temperatures. HPN 20E increased the crystallization temperature up to 129 °C in its mono mixture while it increased the crystallization temperature up to approximately 126 °C in its binary and ternary mixtures as shown in Figure 4.9.

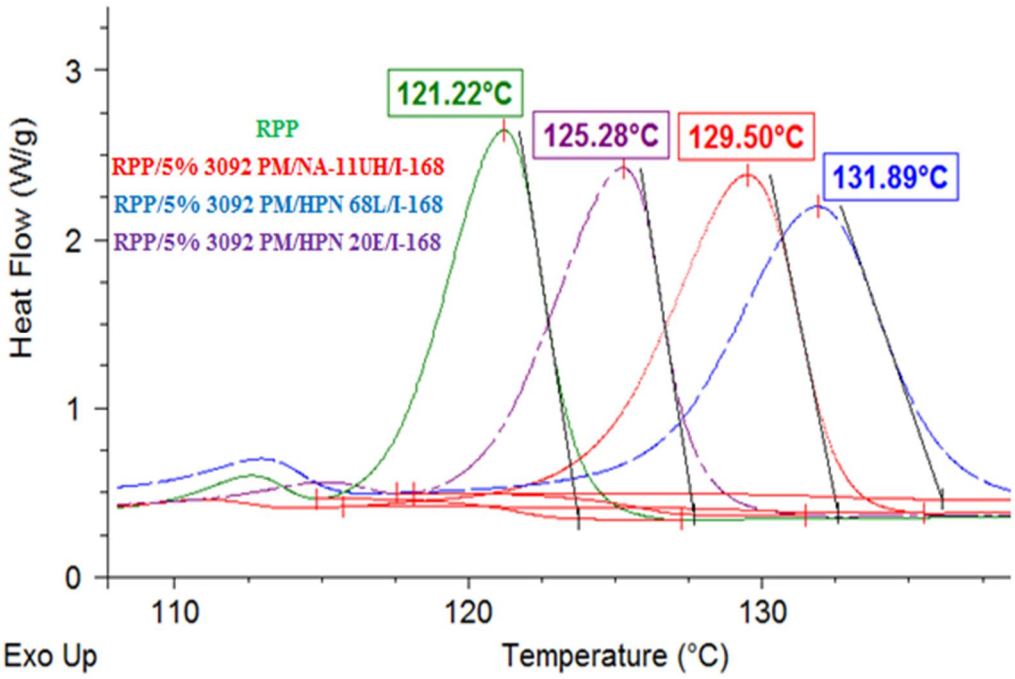

Figure 4.12 : Crystallization peaks of ternary mixtures (with 5% EPDM)

The biggest difference was obtained for all mixtures added HPN 68L. Besides, by the entrance of EPDM to the matrix, crystallization temperature increased at the rate of 2 °C especially for mixtures added HPN 68L as shown in Figure 4.10, 4.11, 4.12, 4.13. In addition, NA-11UH increased crystallization entalphy while HPN 68 L and 20 E either decrased or did not changed it.

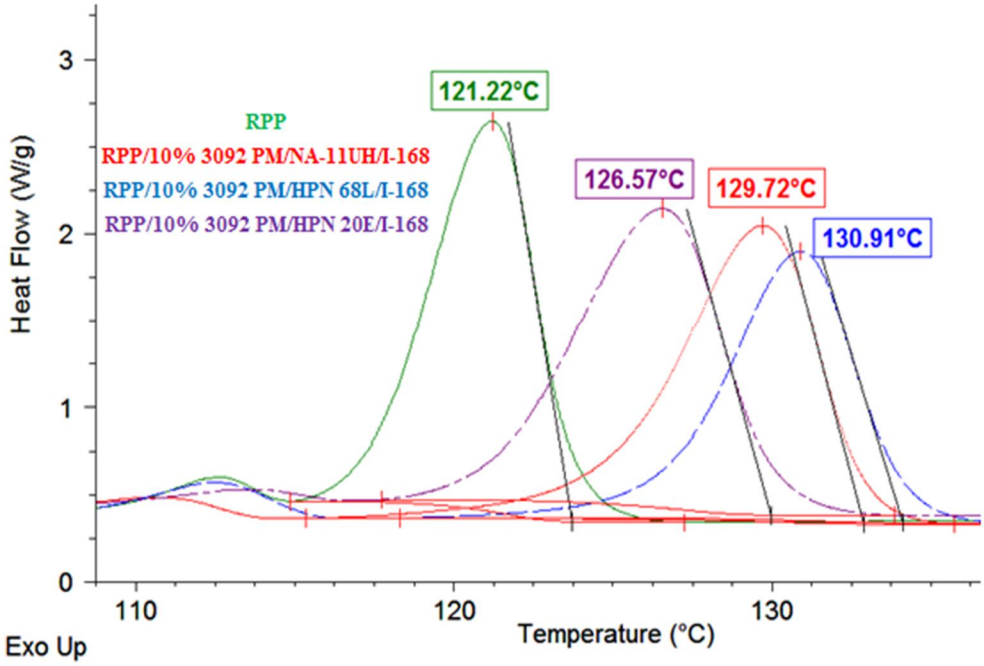

Figure 4.13 : Crystallization peaks of ternary mixtures (with 10% EPDM)

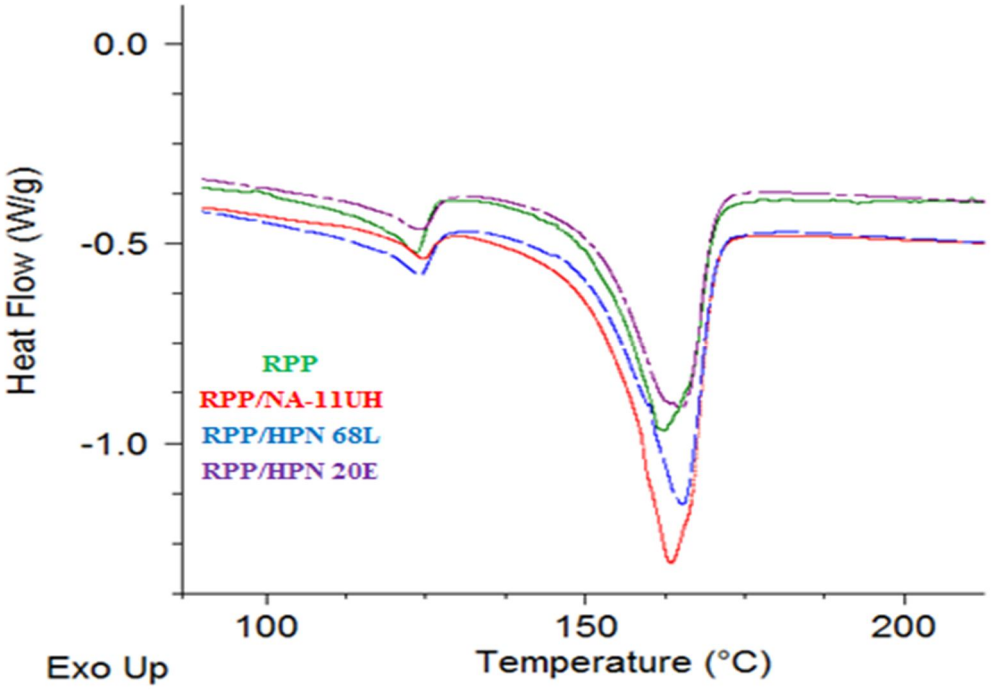

Figure 4.14 : Melting peaks of mono mixtures

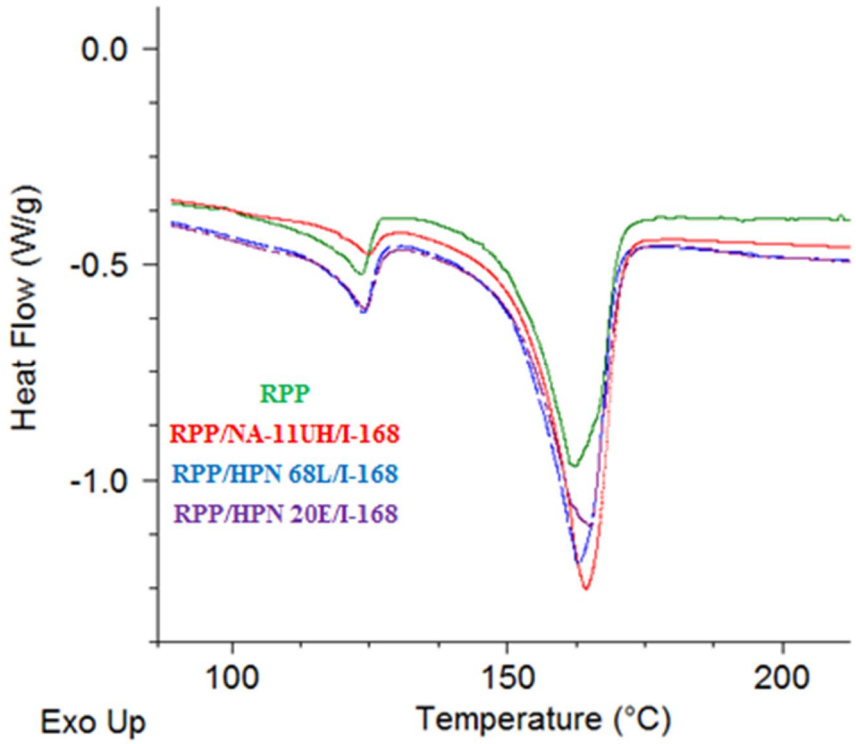

Figure 4.15 : Melting peaks of binary mixtures

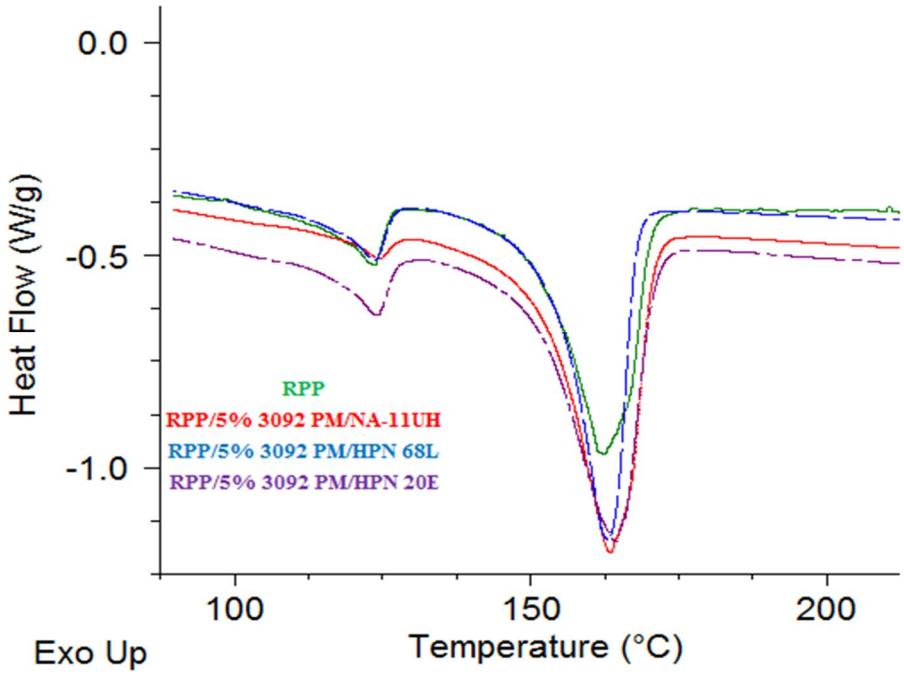

Figure 4.16 : Melting peaks of binary mixtures (with 5% EPDM)

Fusion entalphy was increased compared to RPP. Mono mixtures containing 5% and 10% EPDM had 53.9 J/g and 51.9 J/g, respectively as shown in Table 4.7.

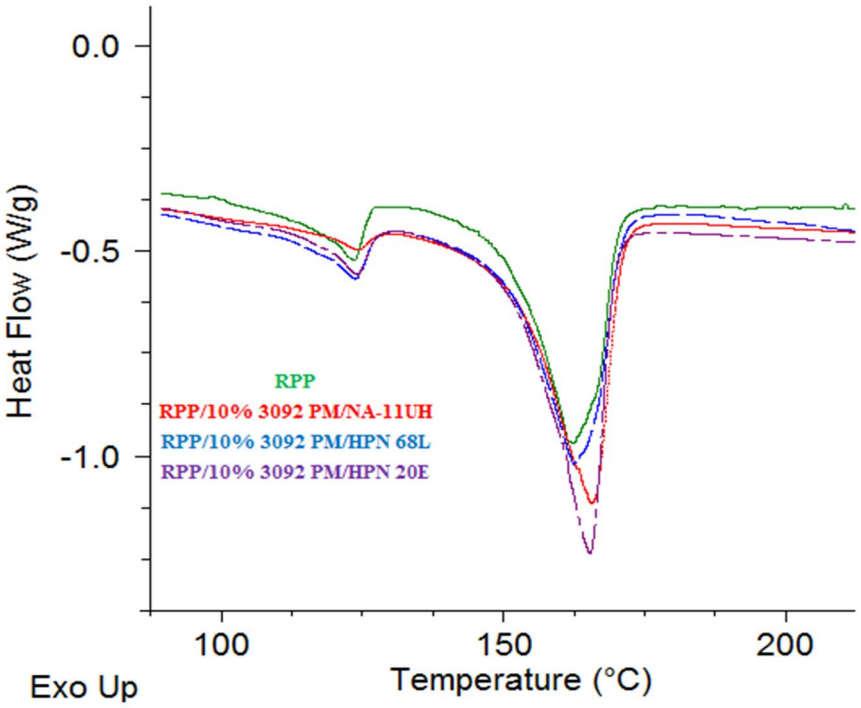

Figure 4.17 : Melting peaks of binary mixtures (with 10% EPDM)

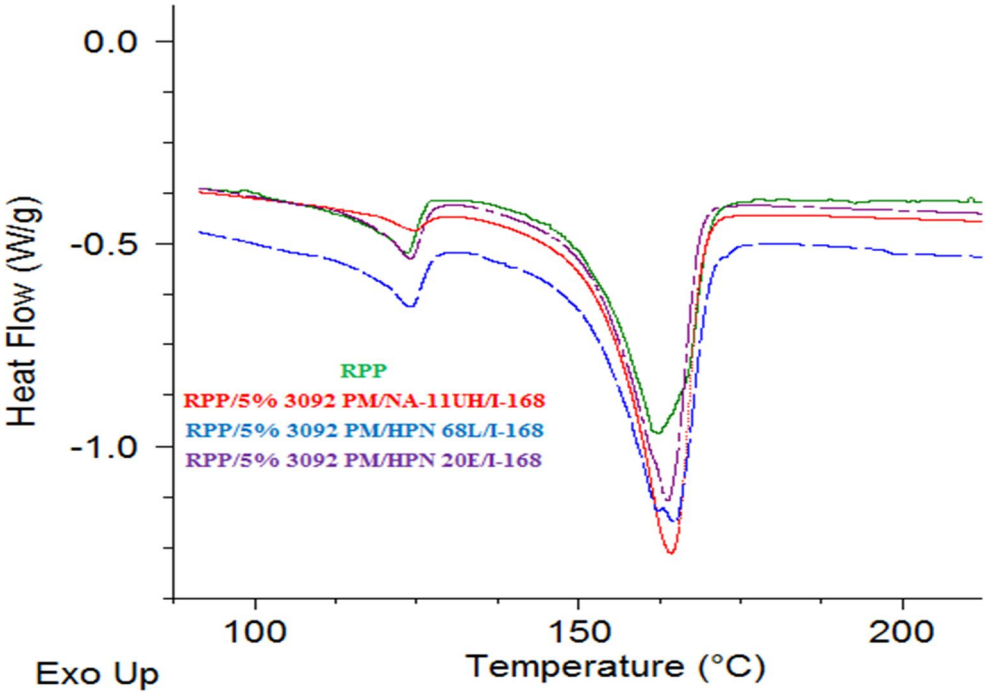

Figure 4.18 : Melting peaks of binary mixtures (with 5% EPDM)

According to results, mixtures added NA-11UH had generally higher entalphy values as shown in Figures 4.14, 4.15, 4.16, 4.18.

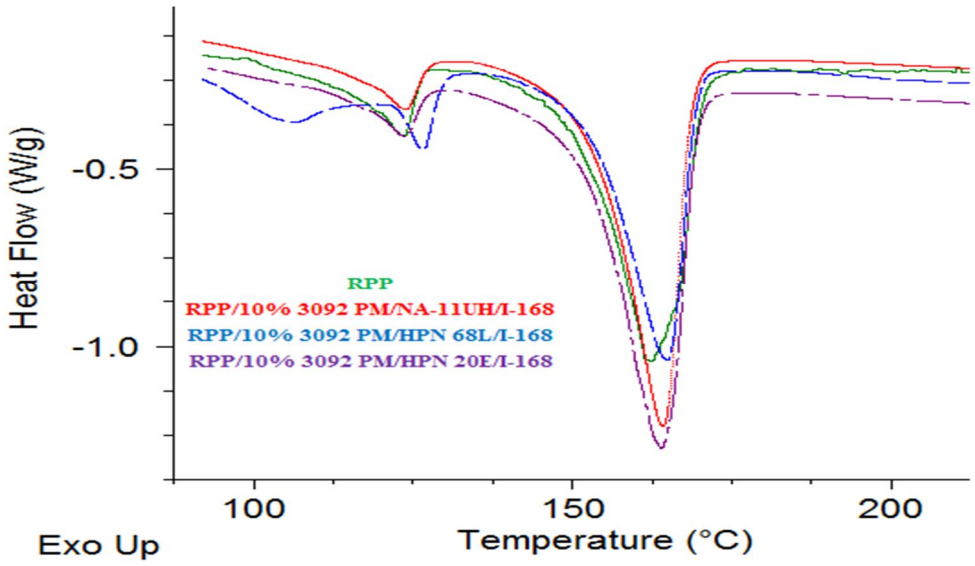

Figure 4.19 : Melting peaks of ternary mixtures (with 10% EPDM)

Table 4.8 : Test results of DSC measurements of the samples

SAMPLES	RPP	3092 PM	NA-11UH	HPN-68L	HPN-20E	Irgafos-168	Tc (onset) (°C)	Tm (onset) (°C)
RPP	100	-	-	-	-	-	124	154
RPP/EPDM	95	5	-	-	-	-	124	154
	90	10	-	-	-	-	124	151
RPP/NA	99.5	-	0.5	-	-	-	133	154
	99.5	-	-	0.5	-	-	132	155
	99.5	-	-	-	0.5	-	133	151
RPP/AO	99.8	-	-	-	-	0.2	124	151
RPP/N.A/AO	99.3	-	0.5	-	-	0.2	133	155
	99.3	-	-	0.5	-	0.2	136	151
	99.3	-	-	-	-	0.2	128	151
RPP/EPDM/NA	94.5	5	0.5	-	0.5	-	133	152
	94.5	5	-	0.5	-	-	135	154
	94.5	5	-	-	0.5	-	129	150
	89.5	10	0.5	-	-	-	133	151
	89.5	10	-	0.5	-	-	136	150
	89.5	10	-	-	0.5	-	130	154
RPP/EPDM/AO	94.8	5	-	-	-	0.2	124	155
	89.8	10	-	-	-	0.2	124	154
RPP/EPDM/NA/AO	94.3	5	0.5	-	-	0.2	133	154
	94.3	5	-	0.5	-	0.2	136	152
	94.3	5	-	-	0.5	0.2	128	152
	89.3	10	0.5	-	-	0.2	133	153
	89.3	10	-	0.5	-	0.2	134	152
	89.3	10	-	-	0.5	0.2	130	153

4.1.5 Polarizing microscopy (POM) analysis

Polarizing microscopy analysis was done as described in section 3.4.1.5. The images of analyses for mono, binary and ternary mixtures were given in Figures 4.20, 4.21, 4.22, 4.23, 4.24, 4.25, 4.26.

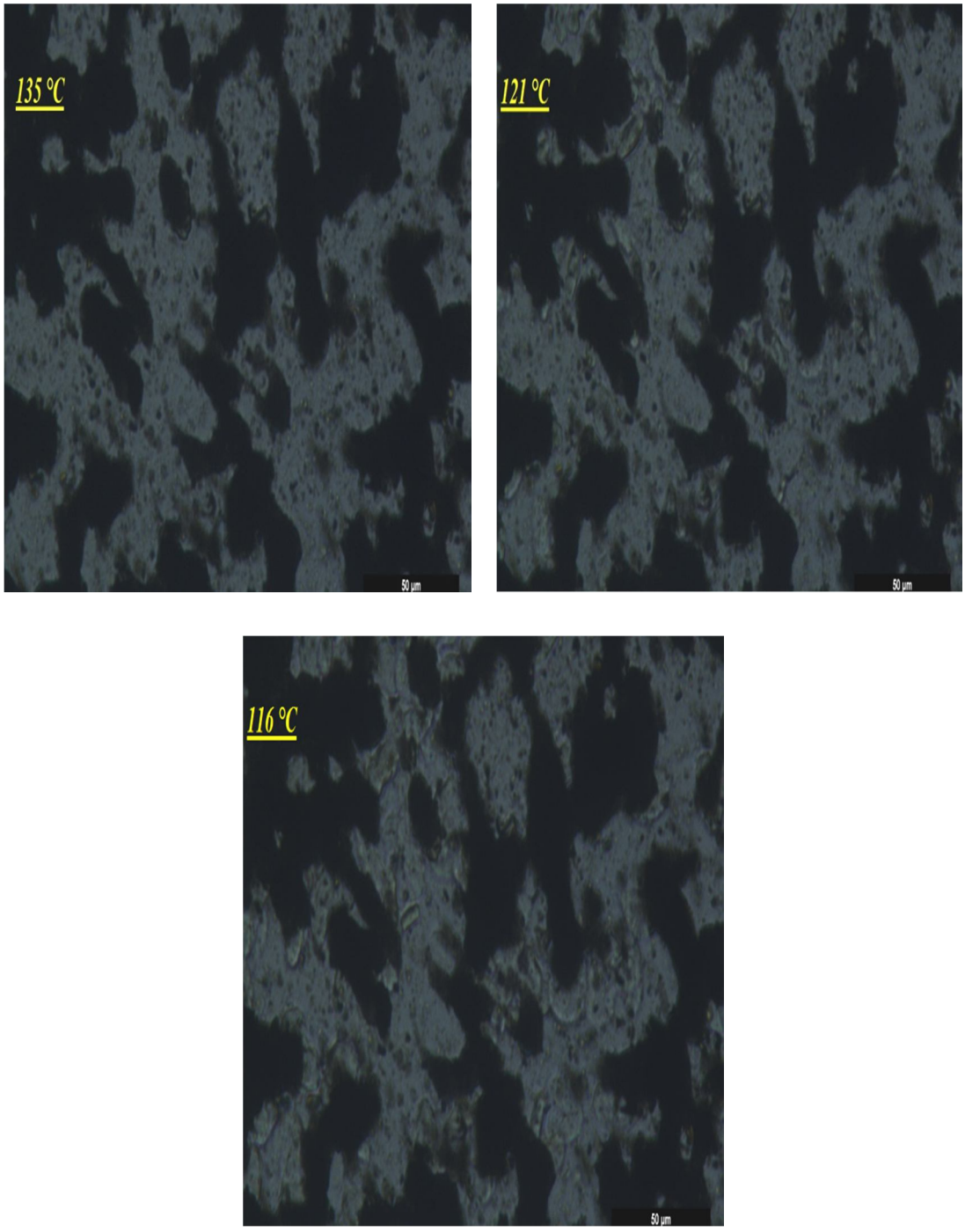

Figure 4.20 : Development of spherulites at 5th (135°C), 19th (121°C), 24th (116°C) minutes at 50µm zoom rate for RPP.

As seen in the DSC diagrams, the additon of nucleating agent changed the initial temperature of crystallization and the size of spherulites. RPP started to crystallize at 121 °C, while nucleated agent added to the mixtures started to crystallize at higher temperatures.

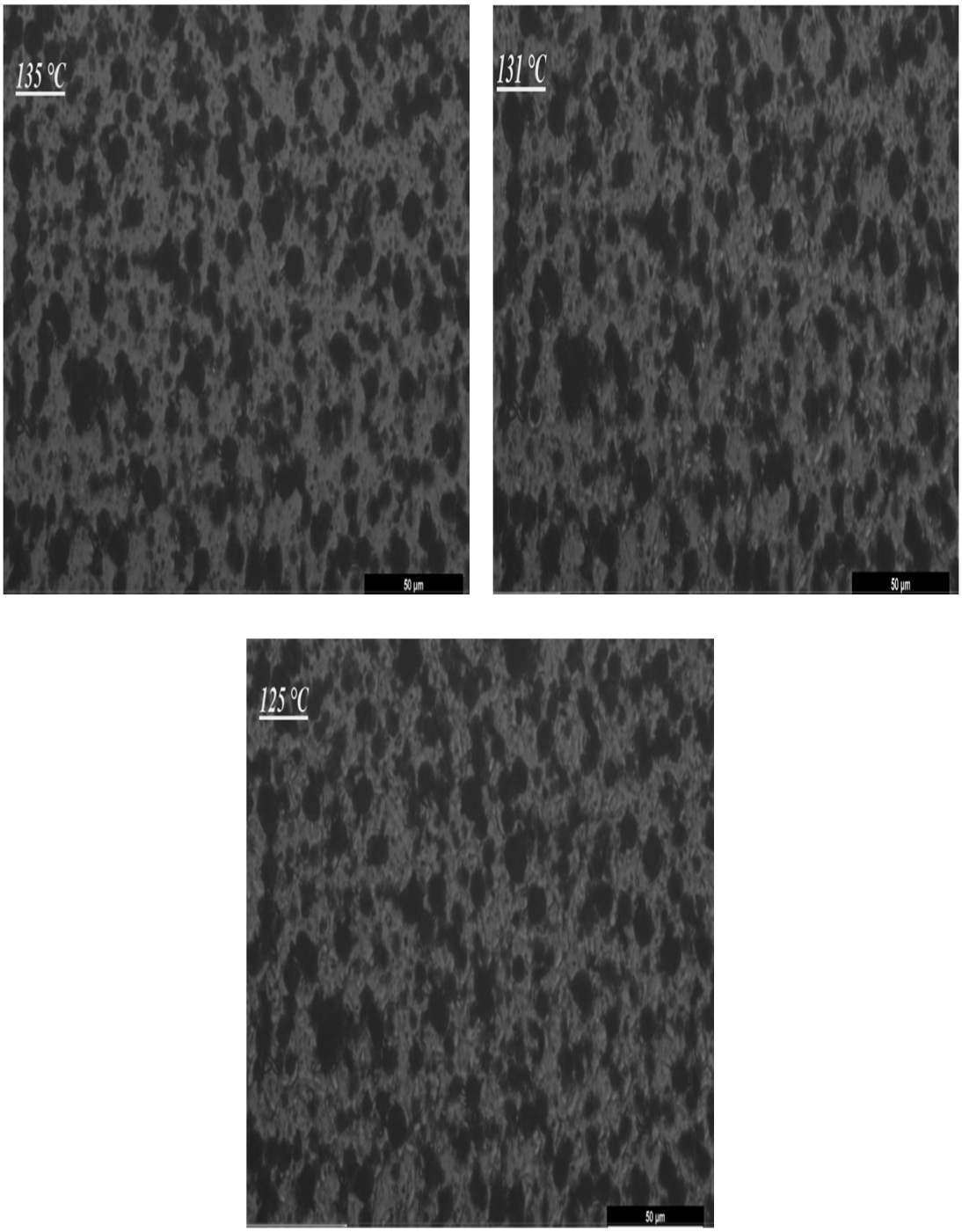

Figure 4.21 : Development of spherulites at 5th (135°C), 9th (131°C), 15th (125°C) minutes at 50µm zoom rate for RPP/NA-11 UH mono mixture

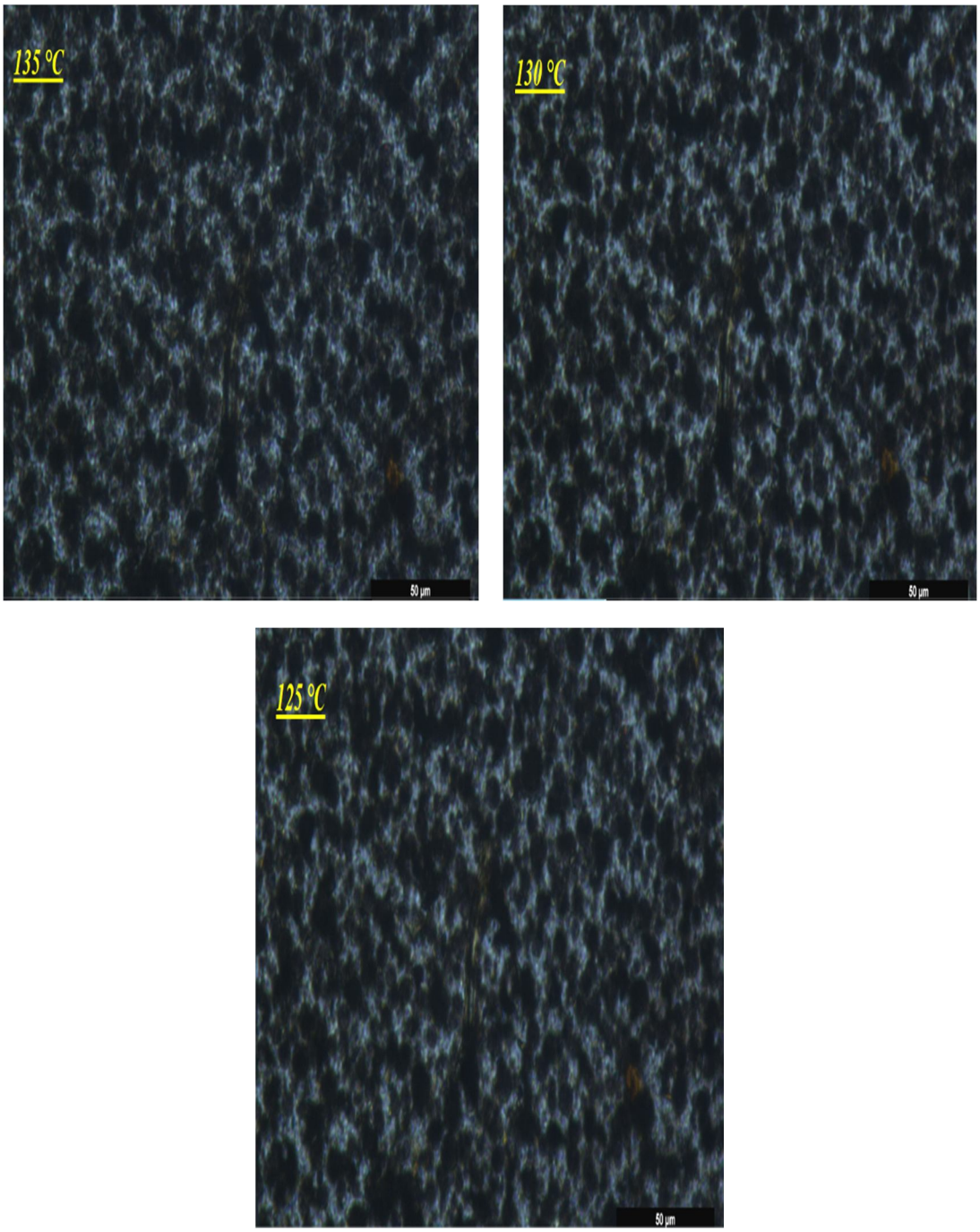

Figure 4.22 : Development of spherulites at 5th (135°C), 10th (130°C), 15th (125°C) minutes at 50µm zoom rate for RPP/ HPN 68L mono mixture

Polarized microscope images were examined in order to observe the spherulite size of samples. Certain differences could not be clearly observed in terms of spherulite sizes among compounds added HPN 68L and HPN 20E.

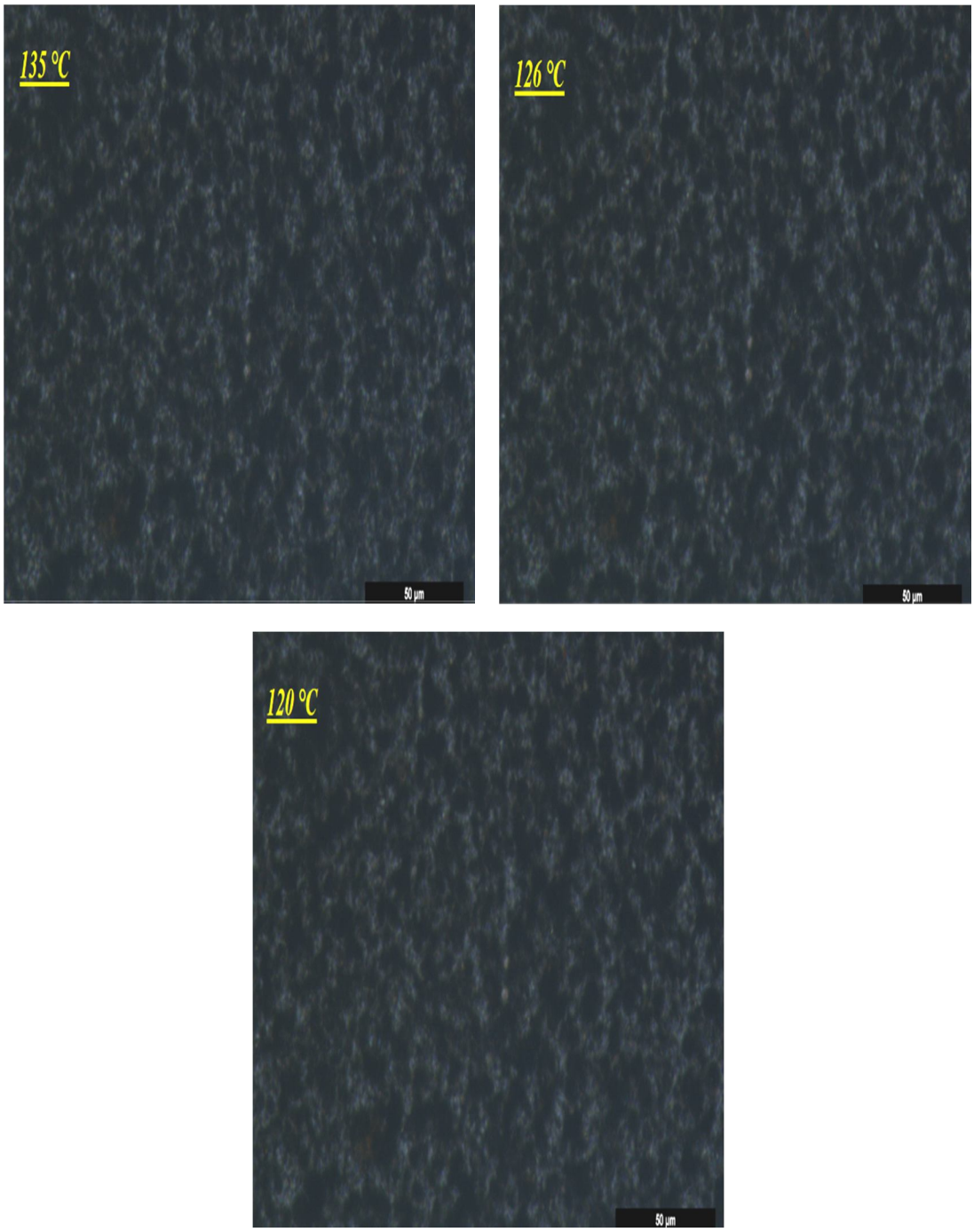

Figure 4.23 : Development of spherulites at 5th (135°C), 14th (126°C), 20th (120°C) minutes at 50µm zoom rate for RPP/ HPN 20E mono mixture

The formation of spherulites was clearly seen in ternary mixture containing NA-11UH as shown in Figure 4.24.

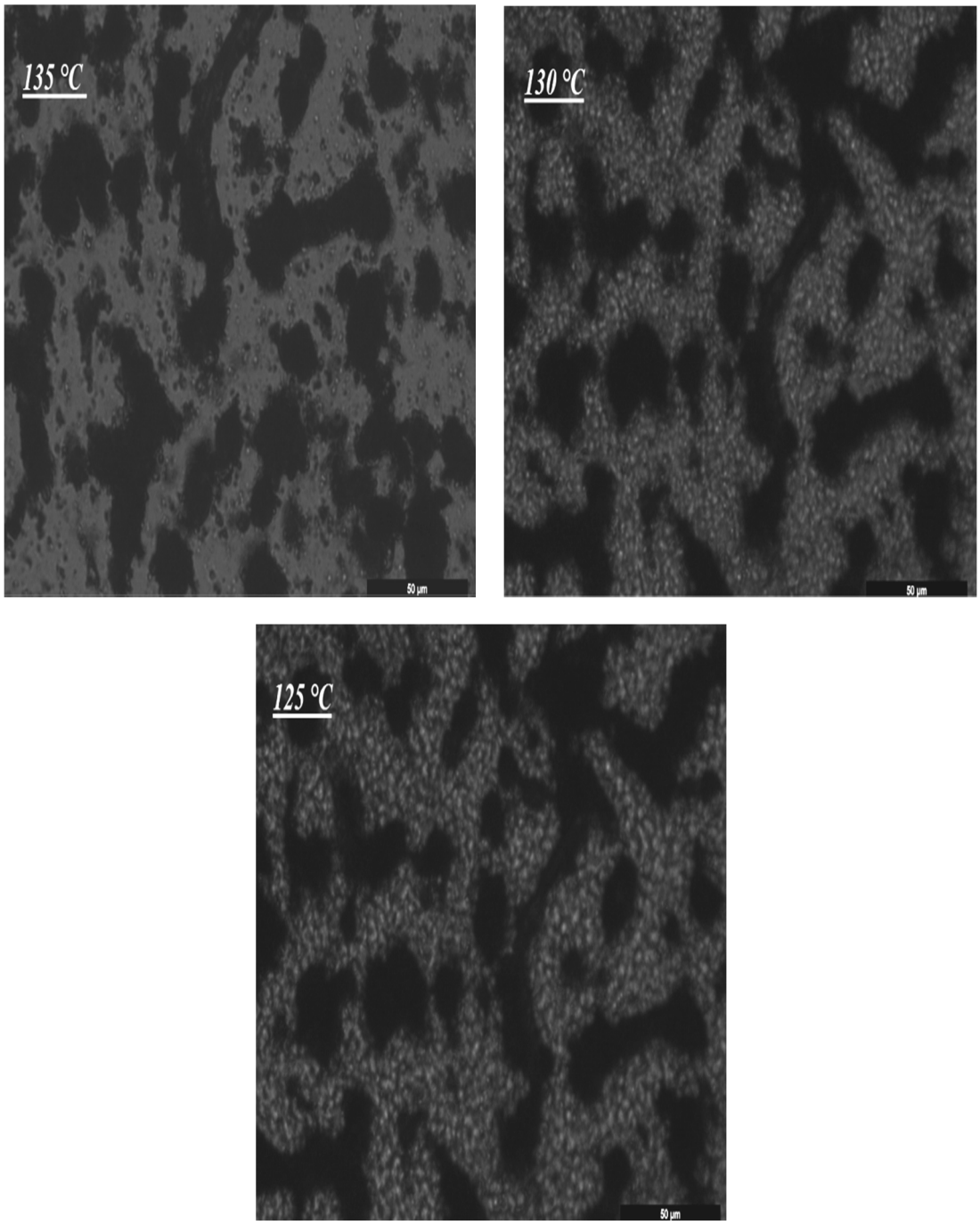

Figure 4.24 : Development of spherulites at 5th (135°C), 10th (130°C), 15th (125°C) minutes at 50µm zoom rate for RPP/NA-11 UH/I-168 ternary mixture

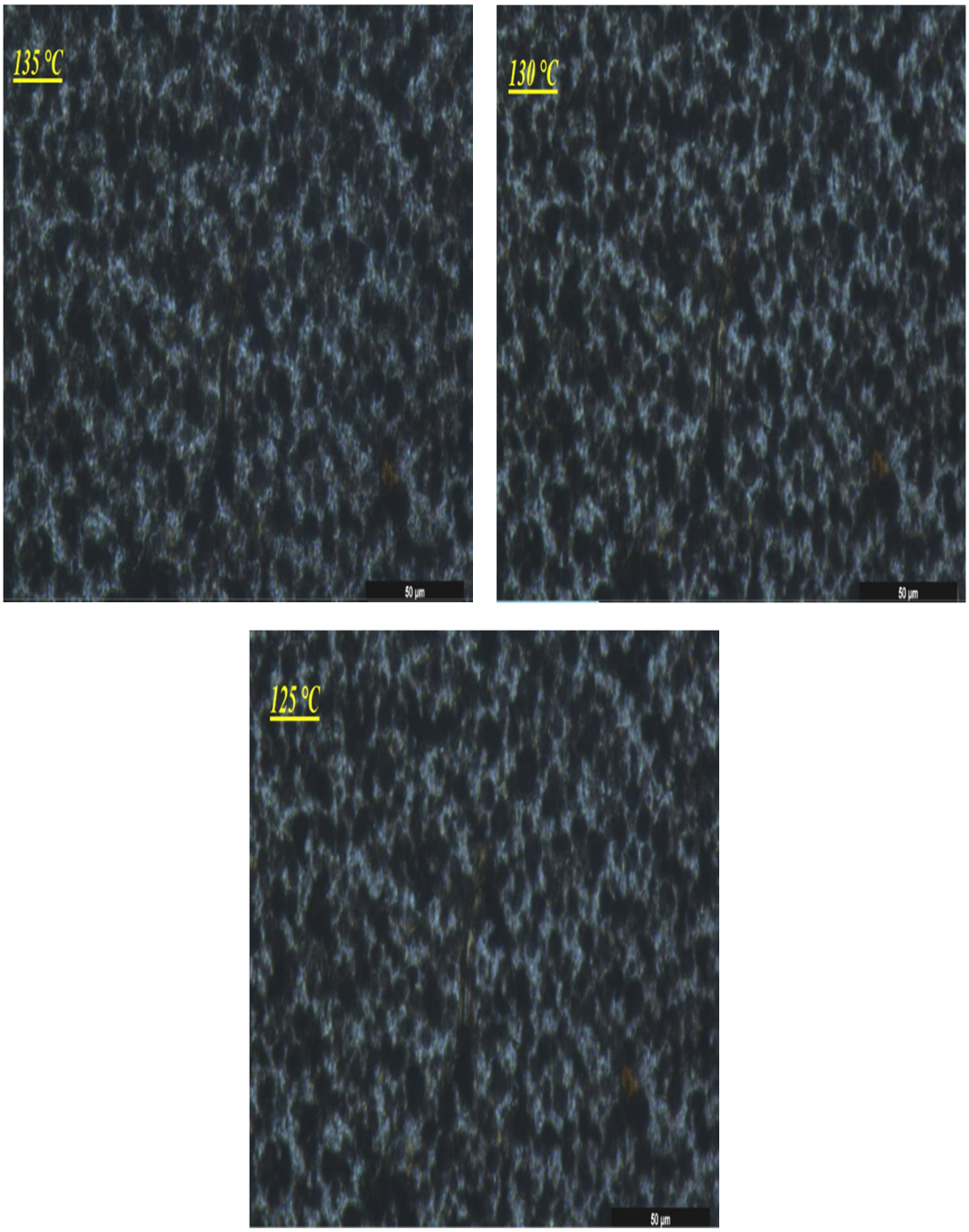

Figure 4.25 : Development of spherulites at 5th (135°C), 10th (125°C), 15th (125°C) minutes at 50µm zoom rate for RPP/HPN 68L/I-168 ternary mixture

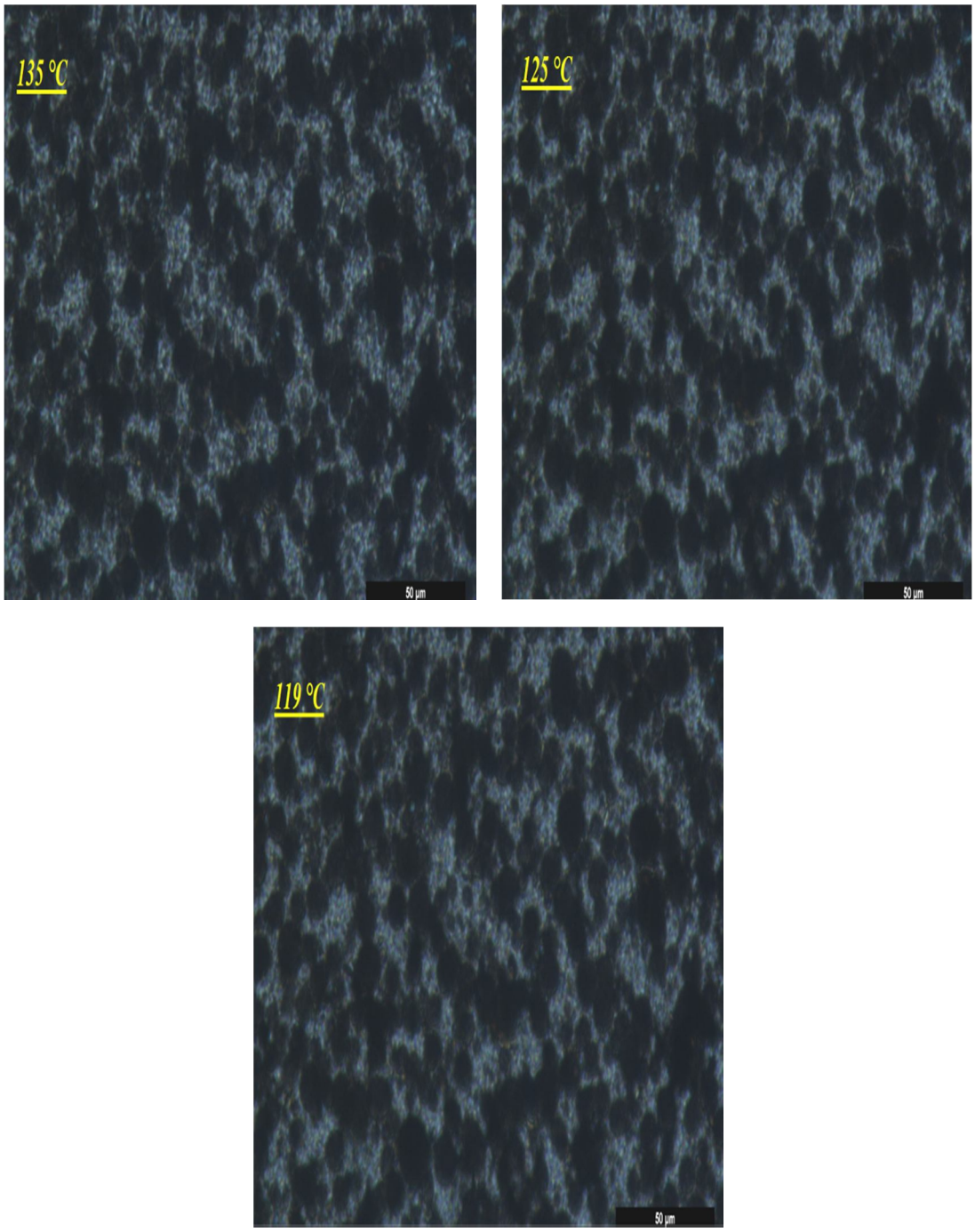

Figure 4.26 : Development of spherulites at 5th (135°C), 15th (125°C), 21th (119°C) minutes at 50µm zoom rate for RPP/HPN 20E/I-168 ternary mixture

4.2 Test Results of Mechanical Properties

Mechanical properties of polypropylene compounds were determined by using mechanical testing methods such as universal testing, Izod impact test, Shore hardness test.

4.2.1 Tensile properties

Tensile test was done according to the procedure explained in section 3.4.2.1. The effects of mono, binary and/or ternary mixtures on tensile strength (MPa), modulus of elasticity (MPa) and percent strain properties of RPP-based compounds were evaluated and test results of all samples are shown in Table 4.8. Tensile strength, elastic modulus and percent strain comparative diagrams according to mono, binary and ternary formulations were presented between Figures 4.27, 4.28, 4.29, 4.30, 4.31, 4.32, 4.33, 4.34. Tensile tests were carried out in order to evaluate effects of varying proportions of EPDM, nucleating agents and antioxidant at different loading levels on the mechanical properties of RPP compounds

Table 4.9 : Test results of tensile testing determination of the samples

SAMPLES	Tensile Strength (Mpa)	Modulus of Elasticity (Mpa)	Strain (%)
RPP	25 ± 2	1210 ± 35	35.6 ± 2.3
RPP/5% EPDM	23 ± 1	960± 67	77.2 ± 1.8
RPP/10% EPDM	20 ± 2	880 ± 78	143.8 ± 0.9
RPP/NA-11UH	25 ± 1	1250 ± 23	31.9 ± 0.5
RPP/HPN 68L	25 ± 1	1260 ± 56	29.5 ± 1.2
RPP/HPN 20E	25 ± 1	1240 ± 40	32.1 ± 1.7
RPP/I-168	25 ± 1	1170 ± 37	22.4 ± 2.1
RPP/NA-11UH/I-168	27 ± 1	1240 ± 97	28.6 ± 3.1
RPP/HPN 68L/I-168	27 ± 2	1280 ± 88	26.7 ± 3.2
RPP/HPN 20E/I-168	26 ± 3	1120 ± 56	31.9 ± 2.4
RPP/5% 3092 PM/NA-11UH	24 ± 3	1070 ± 103	39.5 ± 2.9
RPP/5% 3092 PM/HPN 68L	24 ± 1	1040 ± 96	54.8 ± 1.8
RPP/5% 3092 PM/HPN 20E	22 ± 1	1000 ± 109	67.4 ± 1.5
RPP/10% 3092 PM/NA-11UH	22 ±2	930 ± 123	100.8 ± 0.8
RPP/10% 3092 PM/HPN 68L	22 ± 3	900 ± 76	110.2 ± 0.6
RPP/10% 3092 PM/HPN 20E	21 ± 1	880 ± 103	115.6 ± 0.5
RPP/5% 3092 PM/I-168	23 ± 1	1110 ± 92	98.6 ± 0.3
RPP/10% 3092 PM/I-168	21 ± 1	860 ± 34	165.8 ± 1.1
RPP/5% 3092 PM/NA-11UH/I-168	24 ± 2	1100 ± 45	70.6 ± 1.4
RPP/5% 3092 PM/HPN 68L/I-168	23 ± 1	1050 ± 22	75.7 ± 2.1
RPP/5% 3092 PM/HPN 20E/I-168	23 ± 1	1000 ± 35	76.9 ± 2.7
RPP/10% 3092 PM/NA-11UH/I-168	21 ± 2	980 ± 19	127.6 ± 2.8
RPP/10% 3092 PM/HPN 68L/I-168	21 ± 2	950 ± 28	132.5 ± 2.5
RPP/10% 3092 PM/HPN 20E/I-168	20 ± 1	910 ± 32	141.8 ± 3.4

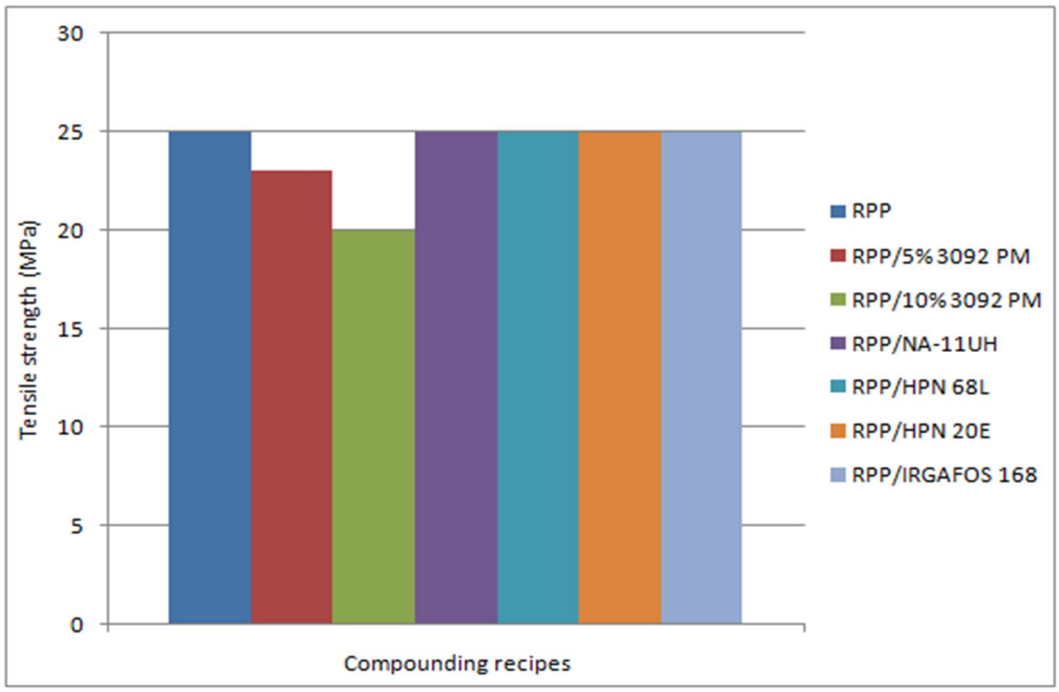

Figure 4.27 : Tensile strength values of mono mixtures

The results showed that tensile strength and elasticity modulus decreased as EPDM was added with 5% and 10%; so percent strain increases compared to RPP as shown in Figures 4.27, 4.30, 4.33. The tensile strength of RPP was around 25 MPa and EPDM decreased tensile strength up to 20 MPa.

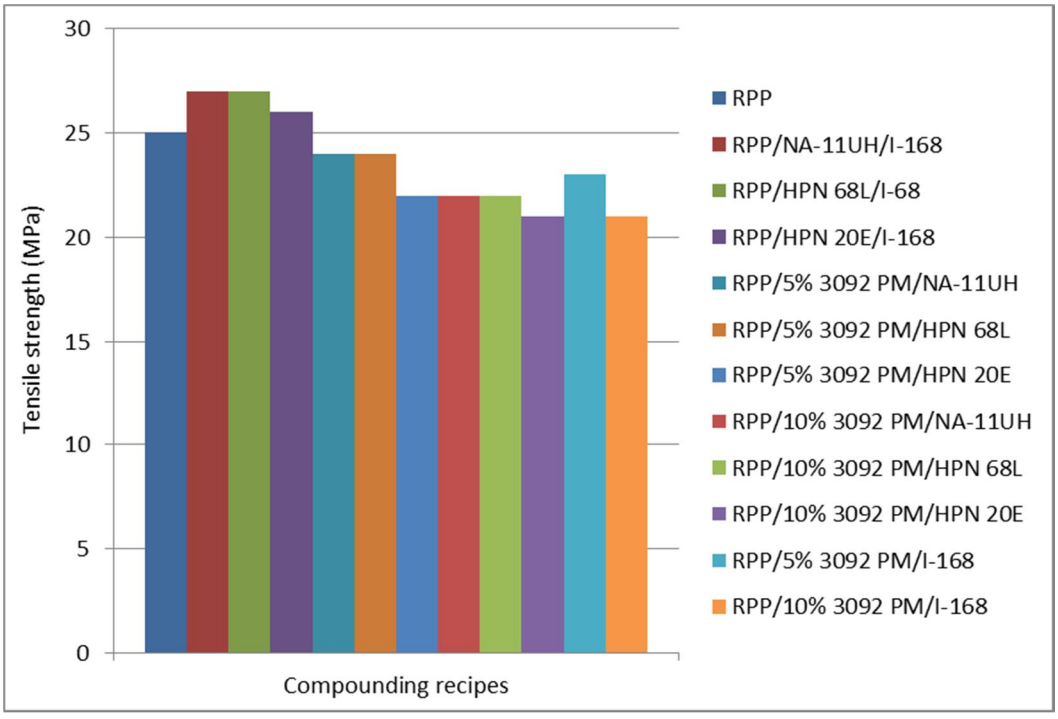

Figure 4.28 : Tensile strength values of binary mixtures

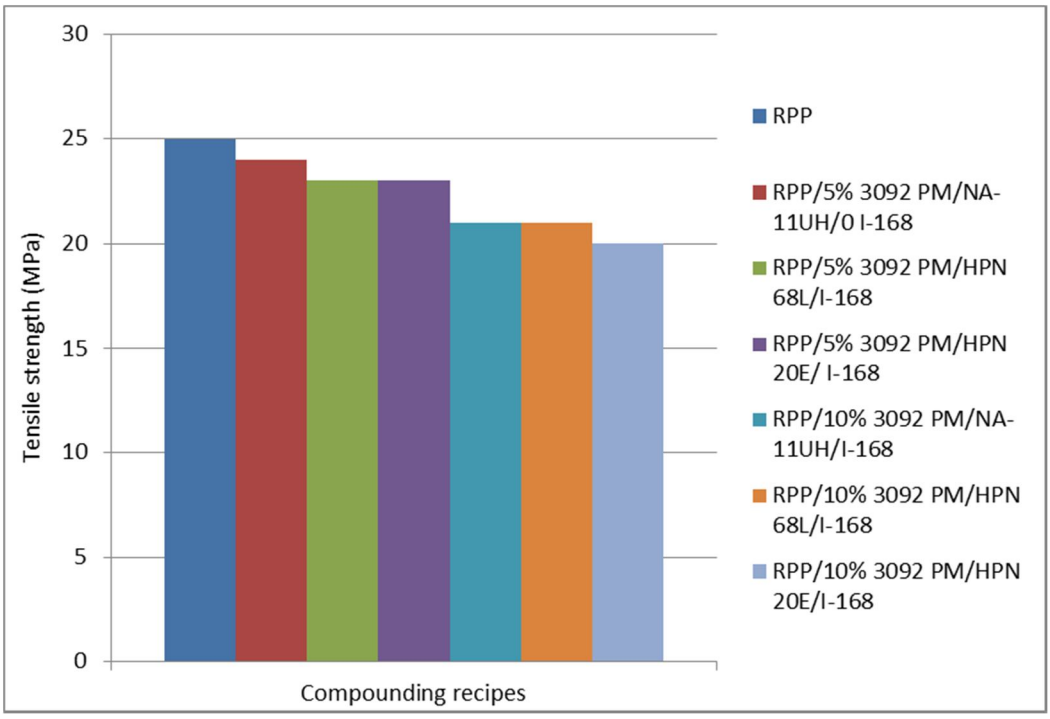

Figure 4.29 : Tensile strength values of ternary mixtures

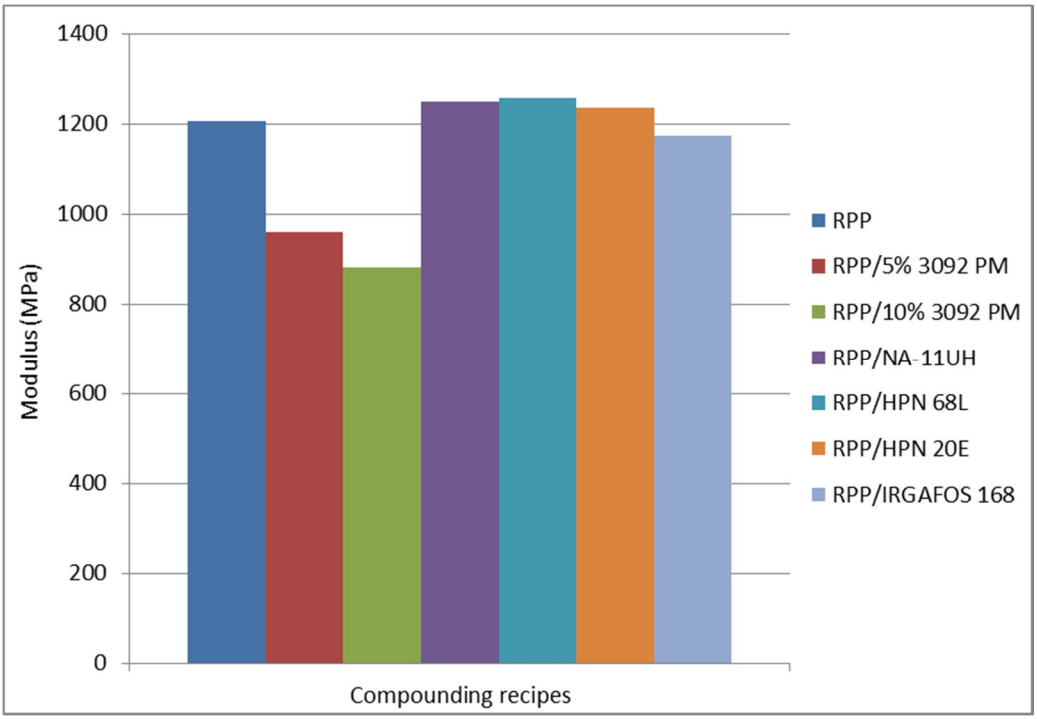

Figure 4.30 : Modulus values of mono mixtures

Similar results were obtained for elastic modulus. The tensile strength of RPP was around 1206 MPa and EPDM decreased tensile strength up to 880 MPa. On the other hand, loading level of 10% by weight of EPDM added compounds had higher

percent strain value such as 143.8% compared to RPP. However, elastic modulus increased by addition of nucleating agents with or without antioxidant, which tended to lower % strain values. The elastic modulus of RPP was 1210 MPa; elastic modulus of nucleated RPP was approximately 1250 MPa.

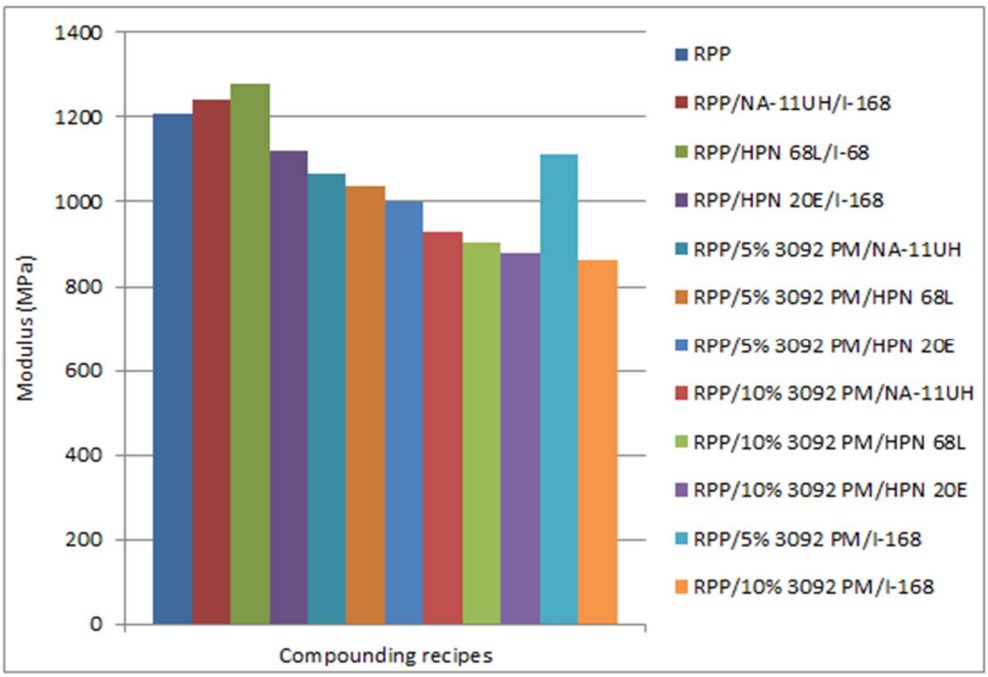

Figure 4.31 : Modulus values of binary mixtures

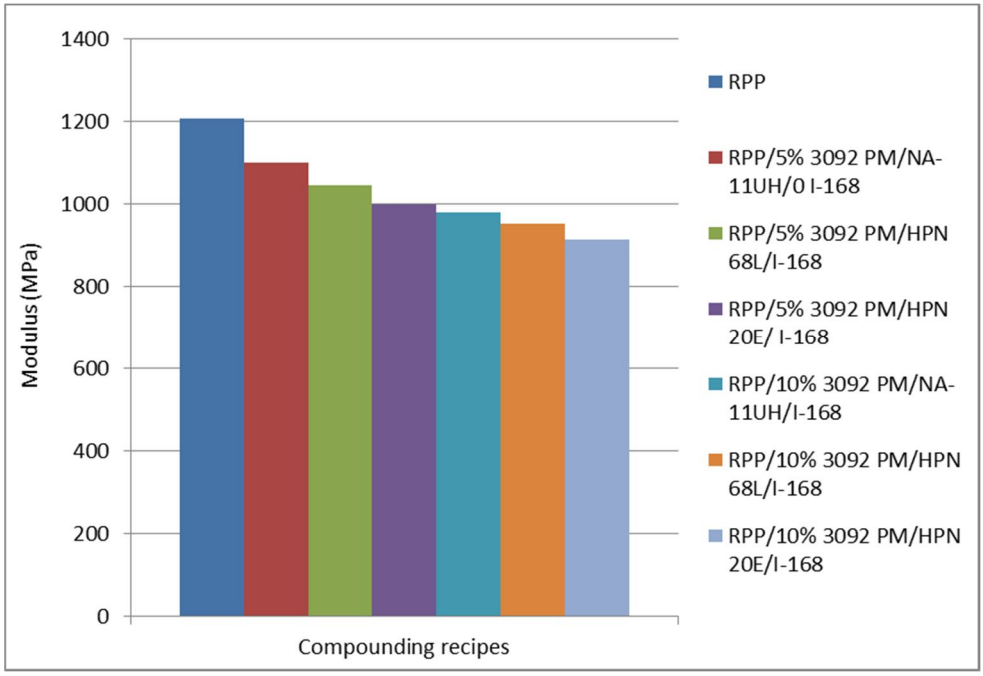

Figure 4.32 : Modulus values of ternary mixtures

EPDM, nucleating agents and antioxidant continued their effects in binary mixtures. The results showed that tensile strength and elastic modulus increased, and so percent strain decreased compared to the results of mono mixtures added EPDM as shown in Figures in 4.28, 4.31, 4.34.

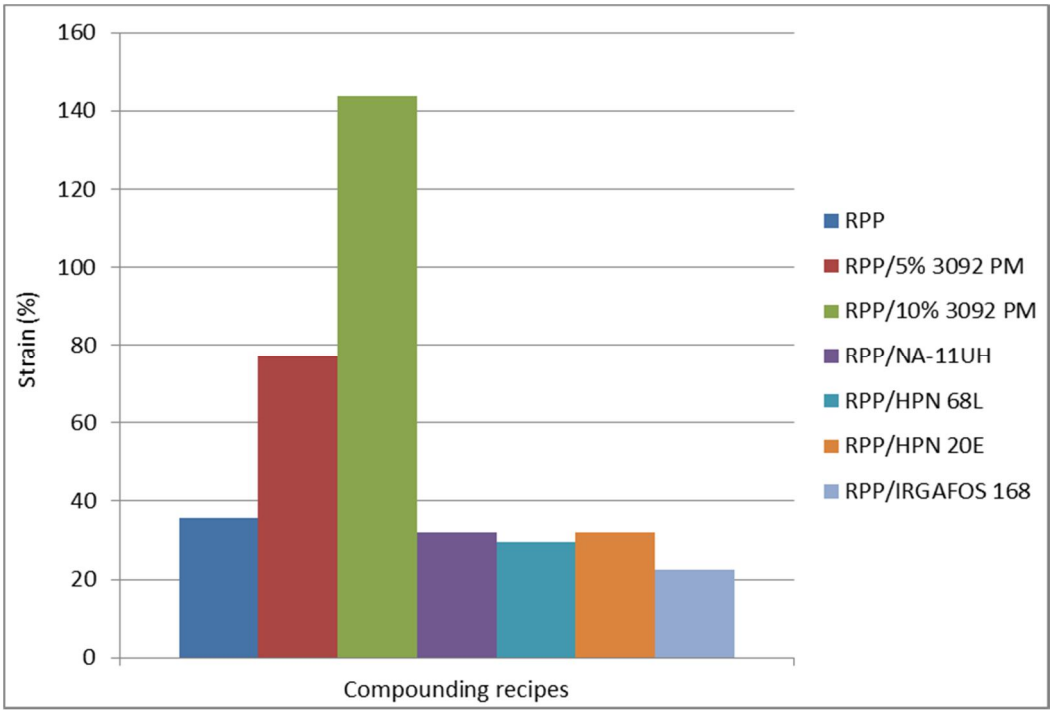

Figure 4.33 : % Strain values of mono mixtures

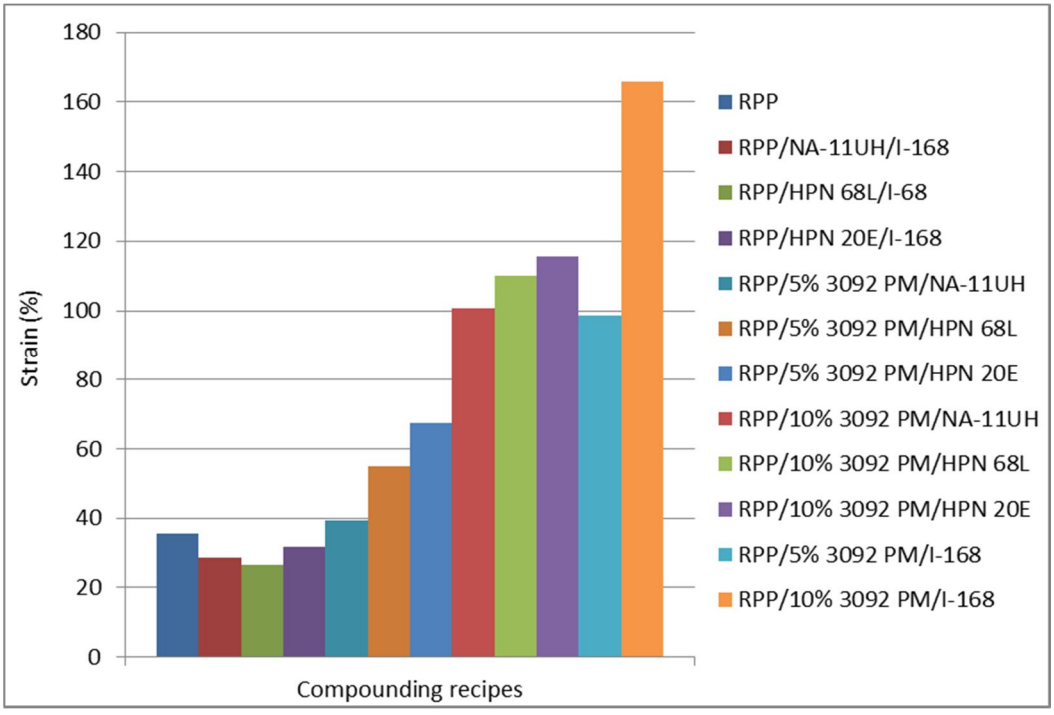

Figure 4.34 : % Strain values of binary mixtures

In ternary mixtures, the differences were observed in especially elastic modulus and percent strain (Figures 4.32, 4.35). The elastic modulus rised up to 980 MPa and percent strain was obtained as 127.6% for RPP/10% 3092PM/NA-11UH/I-168 ternary mixture.

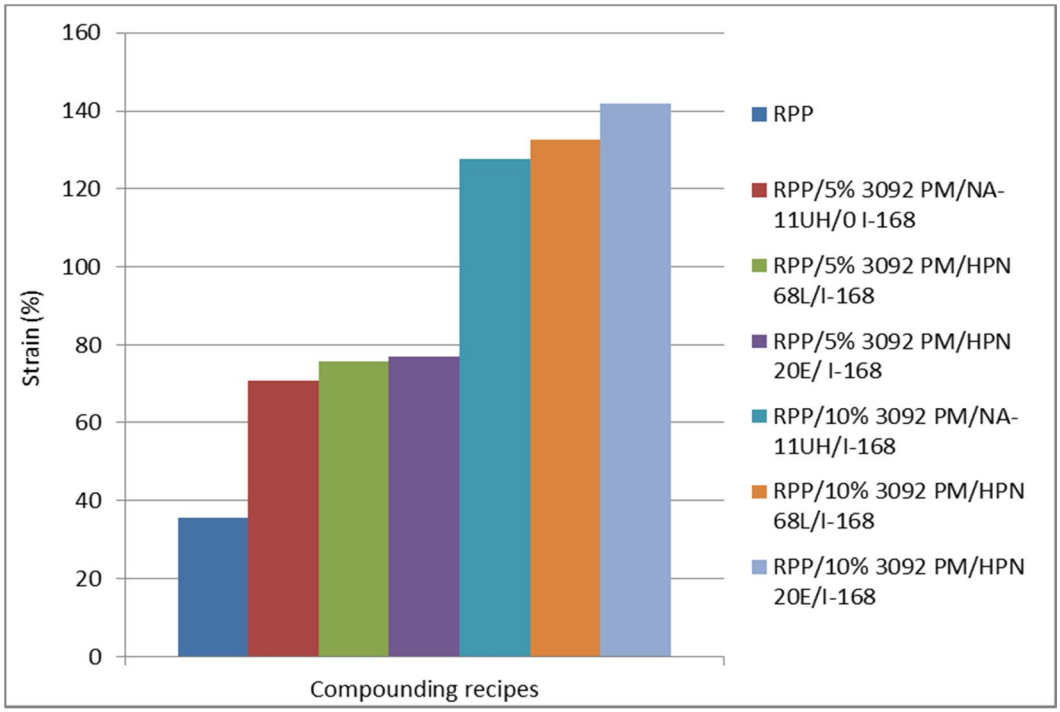

Figure 4.35 : % Strain values of ternary mixtures

4.2.2 Test results of Izod impact strength (E_{Izod})

Izod impact test was done according to the procedure explained in section 3.4.2.2. Izod impact test results are given in Table 4.9. Besides, graphical displays of test results for mono, binary and ternary mixtures were given Figures 4.36, 4.37, 4.38, respectively.

Table 4.10 : Test results of Izod impact testing measurements of the samples

SAMPLES	E_{Izod} (kJ/m^2)
RPP	4.0 ± 0.2
RPP/5% EPDM	6.5 ± 0.2
RPP/10% EPDM	8.9 ± 0.1
RPP/NA-11UH	4.2 ± 0.1
RPP/HPN 68L	4.3 ± 0.1
RPP/HPN 20E	4.1 ± 0.3
RPP/I-168	4.2 ± 0.2
RPP/NA-11UH/I-168	3.6 ± 0.2
RPP/HPN 68L/I-168	3.8 ± 0.1
RPP/HPN 20E/I-168	3.5 ± 0.2
RPP/5% 3092 PM/NA-11UH	6.1 ± 0.2
RPP/5% 3092 PM/HPN 68L	5.8± 0.1
RPP/5% 3092 PM/HPN 20E	5.4 ± 0.2
RPP/10% 3092 PM/NA-11UH	8.4 ± 0.1
RPP/10% 3092 PM/HPN 68L	8.2 ± 0.2
RPP/10% 3092 PM/HPN 20E	7.9 ± 0.2
RPP/5% 3092 PM/I-168	5.7 ± 0.2
RPP/10% 3092 PM/I-168	8.1 ± 0.1
RPP/5% 3092 PM/NA-11UH/I-168	8.5 ± 0.1
RPP/5% 3092 PM/HPN 68L/I-168	8.2 ± 0.2
RPP/5% 3092 PM/HPN 20E/I-168	7.9 ± 0.3
RPP/10% 3092 PM/NA-11UH/I-168	11.8 ± 0.3
RPP/10% 3092 PM/HPN 68L/I-168	11.5 ± 0.2
RPP/10% 3092 PM/HPN 20E/I-168	10.4 ± 0.1

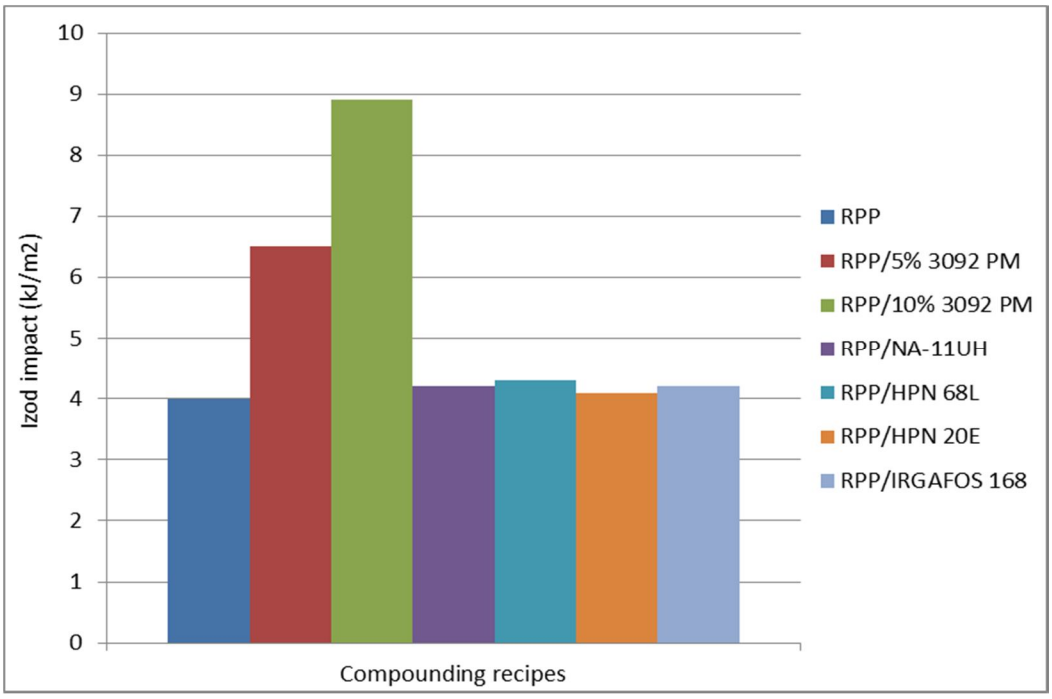

Figure 4.36 : Izod impact strength of mono mixtures

As to Izod impact test results; while EPDM increased impact strength, nucleating agent and antioxidant could not provided enough increase on impact strength in mono mixtures as shown in Figure 4.36. The impact strength (E_{Izod}) of RPP was 4 kJ/m^2 and, this value increased up to 8.9 kJ/m^2 by loading EPDM. But loading nucleating agent slightly changed as approximately 4.2 kJ/m^2.

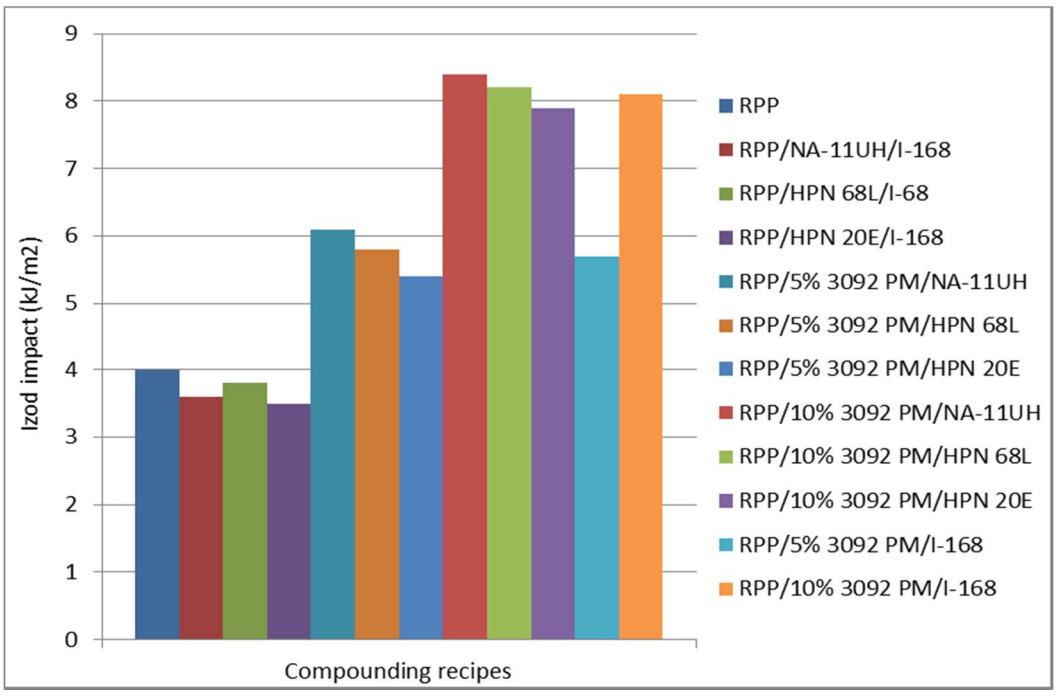

Figure 4.37 : Izod impact strength of binary mixtures

According to the results of binary mixtures; nucleating agents and antioxidant decreased the positive effect of EPDM on impact strength. While EPDM increased impact strength up to 8.9 kJ/m^2, nucleating agents decreaed this value up to approximately 8.2 kJ/m^2.

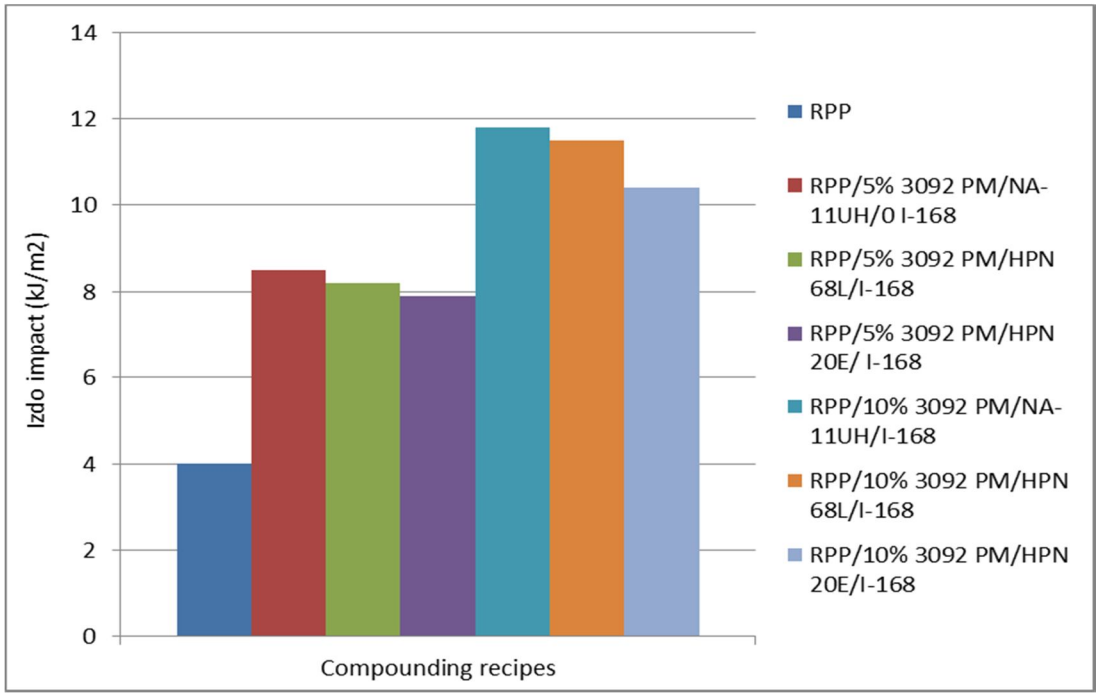

Figure 4.38 : Izod impact strength of ternary mixtures

In ternary mixtures impact strength dramatically increased and a synergic effect was obtained. High values were obtained as 11.8 kJ/m^2, 11.5 kJ/m^2 and 10.4 kJ/m^2 by using NA-11 UH, HPN 68L and HPN 20E, respectively as shown in Figure 4.38.

4.2.3 Test results of Shore-D hardness

Shore-D hardness test was done according to the procedure explained in section 3.4.2.3. Shore-D hardness test results are given in Table 4.10. Besides, graphical displays of test results for mono, binary and ternary mixtures were given Figures 4.39, 4.30, 4.31, respectively. Shore-D hardness test were carried out in order to evaluate effects of varying proportions of EPDM, nucleating agents and antioxidant on the hardness property of RPP compounds.

Table 4.11 : Test results of Shore-D hardness measurements of the samples

SAMPLES	Hardness (Shore D)
RPP	72±1
RPP/5% EPDM	67±1
RPP/10% EPDM	68±1
RPP/NA-11UH	72±1
RPP/HPN 68L	73±1
RPP/HPN 20E	73±1
RPP/I-168	73±1
RPP/NA-11UH/I-168	73±1
RPP/HPN 68L/I-168	74±1
RPP/HPN 20E/I-168	74±1
RPP/5% 3092 PM/NA-11UH	71±1
RPP/5% 3092 PM/HPN 68L	72±1
RPP/5% 3092 PM/HPN 20E	72±1
RPP/10% 3092 PM/NA-11UH	69±1
RPP/10% 3092 PM/HPN 68L	70±1
RPP/10% 3092 PM/HPN 20E	70±1
RPP/5% 3092 PM/I-168	71±1
RPP/10% 3092 PM/I-168	70±1
RPP/5% 3092 PM/NA-11UH/I-168	71±1
RPP/5% 3092 PM/HPN 68L/I-168	72±1
RPP/5% 3092 PM/HPN 20E/I-168	72±1
RPP/10% 3092 PM/NA-11UH/I-168	70±1
RPP/10% 3092 PM/HPN 68L/I-168	71±1
RPP/10% 3092 PM/HPN 20E/I-168	71±1

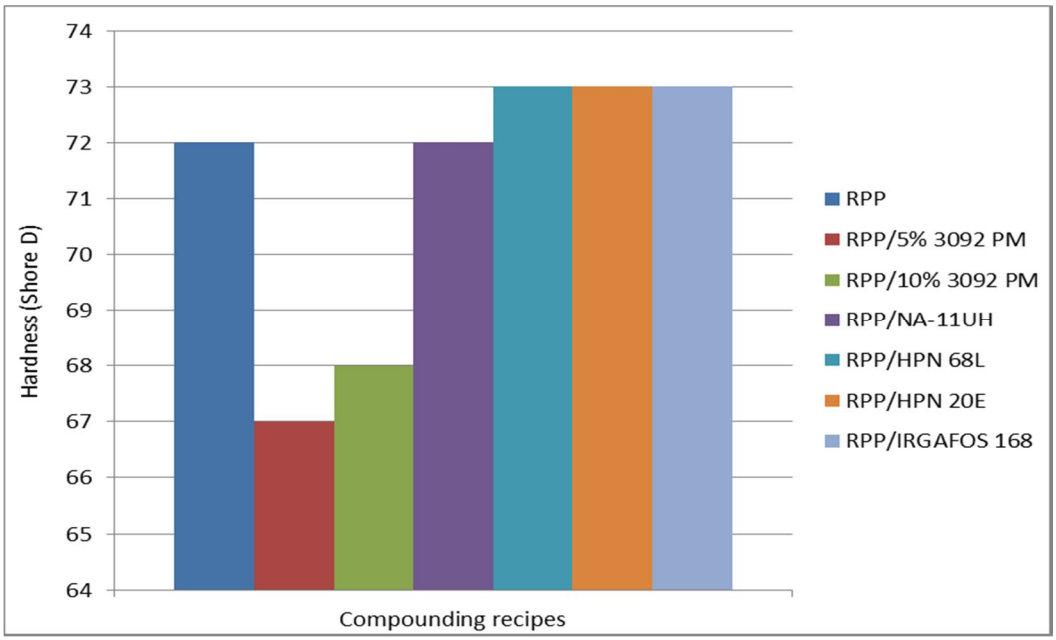

Figure 4.39 : Shore-D hardness of mono mixtures

The results showed that hardness decreased as EPDM was added with 5% and 10%. While the hardness value of RPP was 72 Shore-D, compound added 10% EPDM had 67 Shore-D hardness. In mono mixtures, both nucleating agents and antioxidant incerased the hardness value. In binary and ternary mixtures, nucleating agents and antoxidant similarly increased Shore-D hardness value in comparison with mono mixtures added merely EPDM.

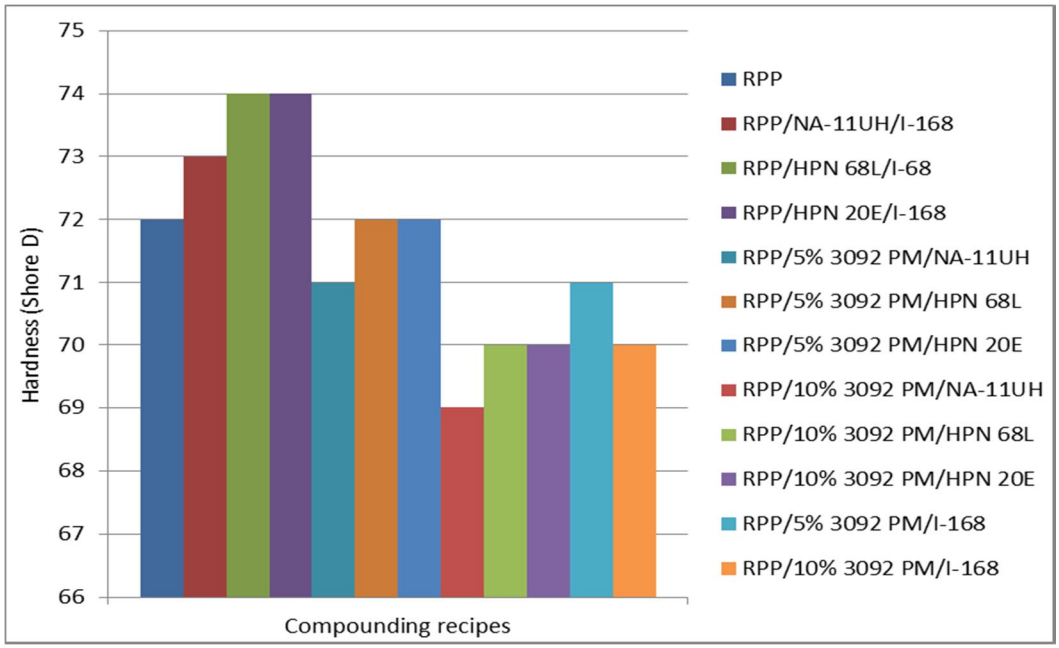

Figure 4.40 : Shore-D hardness of binary mixtures

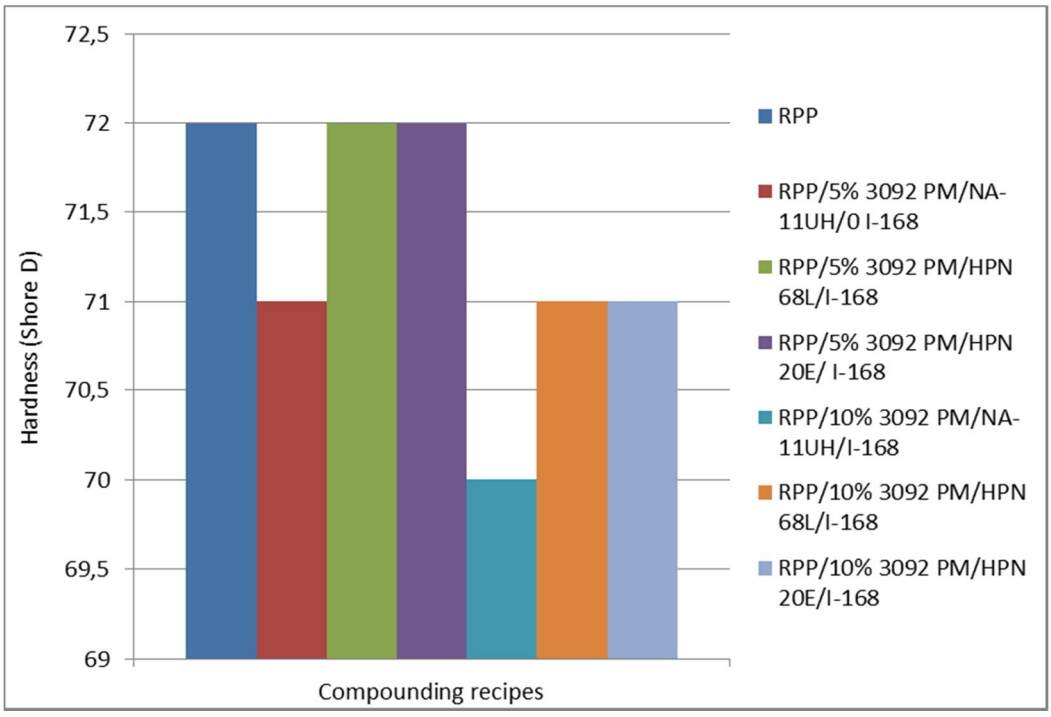

Figure 4.41 : Shore-D hardness of ternary mixtures

5. CONCLUSION

In this study, mono, binary and ternary mixtures were prepared in order to observe effects of elastomeric additive, α-NAs and antioxidant on recycled PP by using compounding method. The raw materials were firstly pre-mixed and then compounded in the co-rotating extruder. Screw speed was determined as 500 rpm in order to disperse EPDM and suitable temperature profile was used for RPP. For the preparation of the samples, all the process parameters were kept constant in order to prevent the additional effects.

Density measurements showed that there was not any difference between the mixtures that contains EPDM, nucleating agent and antioxidant. RPP has a density of 0.92 g/cm3 and compounds containing EPDM/N.A/A.O have approximately 0.93 or 0.94 g/cm3, so that the results indicated that there were no significant differences for compunds based-RPP in terms of density values. The most remarkable result here, the density value of RPP is higher than that of virgin PP due to presence of some inorganic additives from its previous production.

Rheological properties were affected by the addition of EPDM into matrix at different loading levels. The results indicated that the melt flow index (MFI) values decreased significantly with increasing loading level of EPDM. RPP has a MFI value of 15 g/10 min. The highest loading of 10 wt% EPDM decreased MFI up to 8.1 g/10 min. By the inclusion of EPDM to the matrix the melt flow index values decreased due to decreasing of chain movements of RPP. However, nucleating agent or antioxidant did not cause any differences on MFI.

The effects of nucleating agents on crystallization behaviour were investigated based on XRD results. α-nucleated RPP samples show monoclinic α-form at the diffraction angles 2θ = 14.1°, 16.9°, 18.5°, 21.2° [40,41]; and these diffraction angles were seen in compounds containing HPN 68L or HPN 20E. Besides, α-NAs dramatically changed intensity corresponding to "θ" angles of recycled PP in ternary mixtures. This result showed that ternary compounds provided more durable crystal structures on recycled PP.

Mechanical property analysis of the samples showed that espacially ternary mixtures had a pronounced effect on the tensile properties of these materials. Mechanical results showed that tensile strength and elastic modulus decreased with increasing loading level of EPDM. The tensile strength and elastic modulus of recycled PP was around 25 MPa and 1210 MPa, respectively. Tensile strengths decreased to 20 MPa by adding 10% EPDM. Besides, percent strain values increased to 143.8% by EPDM addition. On the other hand, loading of nucleating agent caused adverse effect compared to EPDM. Shore-D hardness measurements results showed that the loading of EPDM decreased hardness.

At this point; impact, tensile test and hardness results should be evaluated together in order to emphasise the effect of synergic effects between additives. The high impact strength obtained by using EPDM could not be seen when only nucleating agent was used in mixtures. The high tensile strength, elastic modulus and hardness values were obtained by using nucleating agents, but in the same mixtures very low impact strength values were seen. At the same time, binary mixtures containing nucleating agent or antioxidant had high tensile strength, elastic modulus and hardness, which tended to lower percent strain and impact strength values. Besides, impact strength increased with ternary mixtures compared to mono mixtures containing merely EPDM. Especially the usage of NA-11 UH with EPDM provided the most distinct effect. In brief; the usage of ternary mixtures provided that both high impact resistance and also high tensile properties when recycled polypropylene was evaluated as engineering plastic.

DSC diagrams showed that recycled PP contains 5% polyethylene. This detail is actually very important point in terms of mechanical properties and the usage of EPDM. It was seen that, the presence of polyethylene and EPDM in structure of compound caused higher mechanical properties such as tensile and impact results. During compounding process, between interaction is obtained between polyethylene and EPDM. Thus, this situation affects mechanical property results.

In the DSC results, the effect of α-NAs was observed clearly in terms of crystallization behaviour. The crystallization temperature increased by adding nucleating agent from 121.2 °C to 131.8 °C. This effect was also obtained from POM images. While crystallization recycled PP started at 19^{th} (121°C); formulations added α-NAs started to crystallize earlier; at nearly 9^{th} and 10^{th}. The most effect was

observed by using HPN 68L. Besides, the effect of α-NAs in terms of spherulite size was observed with POM images. The spherulite size of recycled PP was bigger than α-nucleated ones. The most distinct image in terms of crystallization formation was obtained with the POM image in RPP/10% 3092PM/NA-11UH/I-168 ternary mixture. This may be an indicator why the best mechanical results obtained by using NA-11UH.

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APPENDICES

APPENDIX A.1 : Diagrams of X-ray Diffraction (XRD) Analysis
APPENDIX A.2 : Diagrams of Differential Scanning Calorimetry (DSC) Analysis

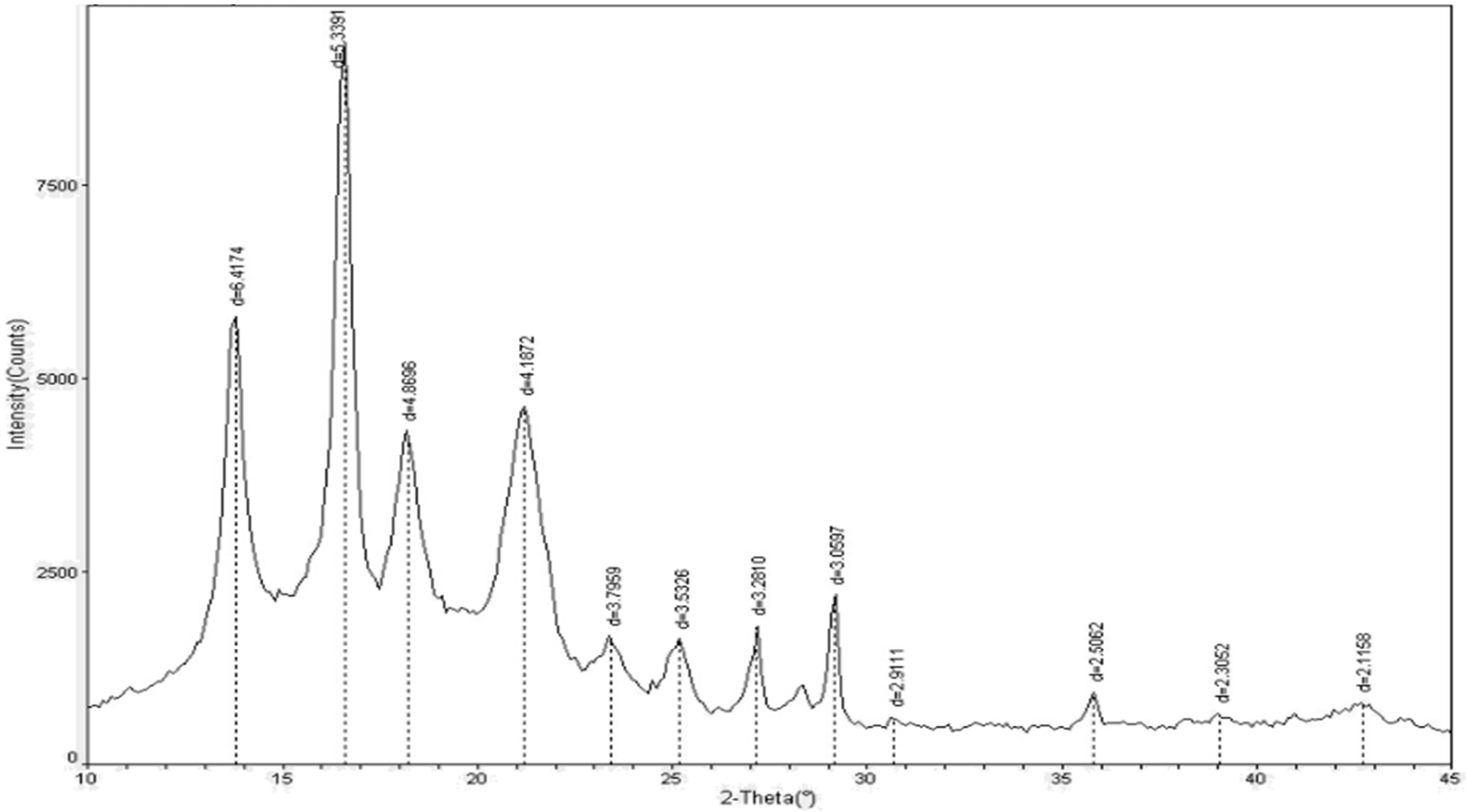

Figure A.1.1 : XRD diagram of RPP

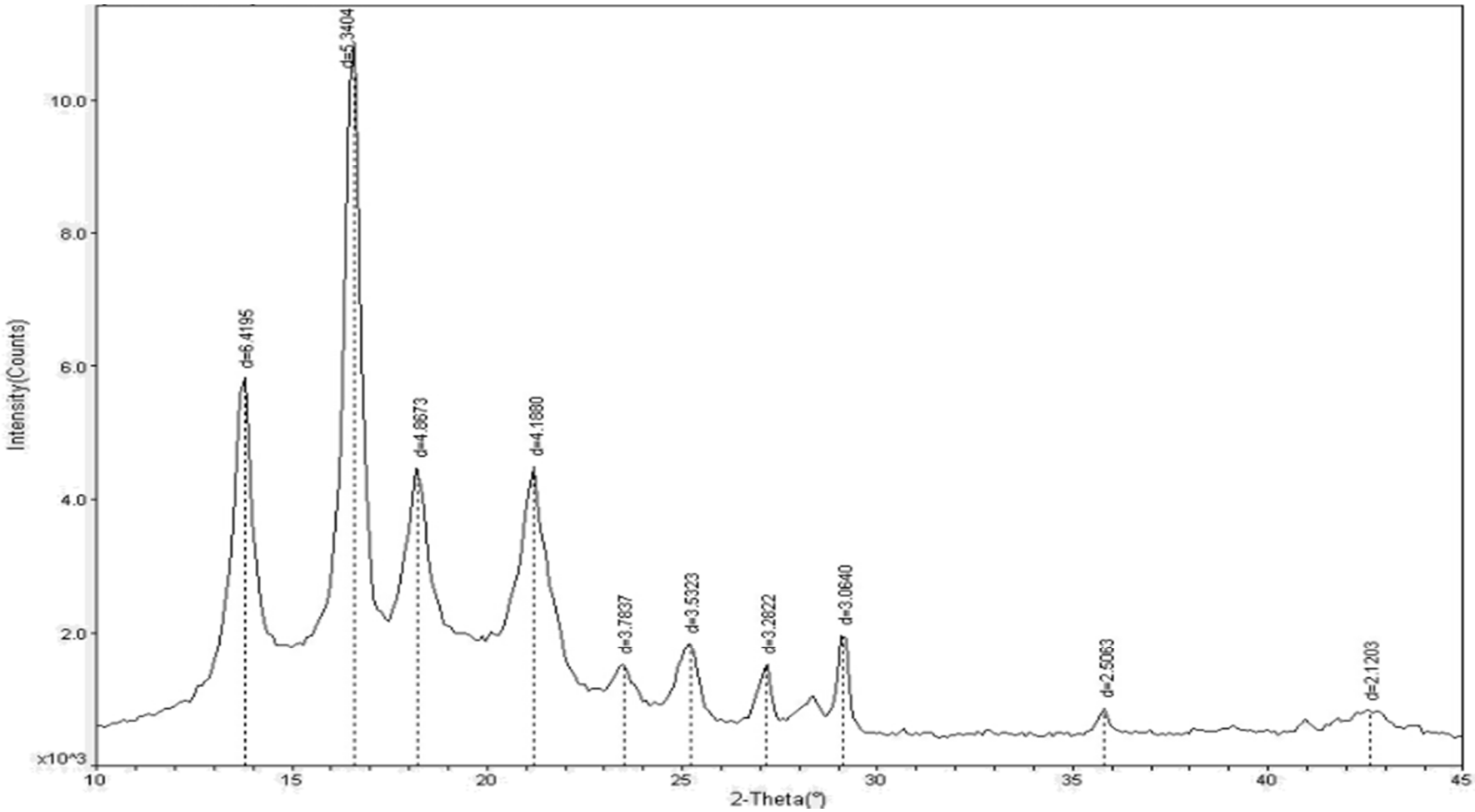

Figure A.1.2 : XRD diagram of RPP/5%EPDM/NA-11UH/I-168

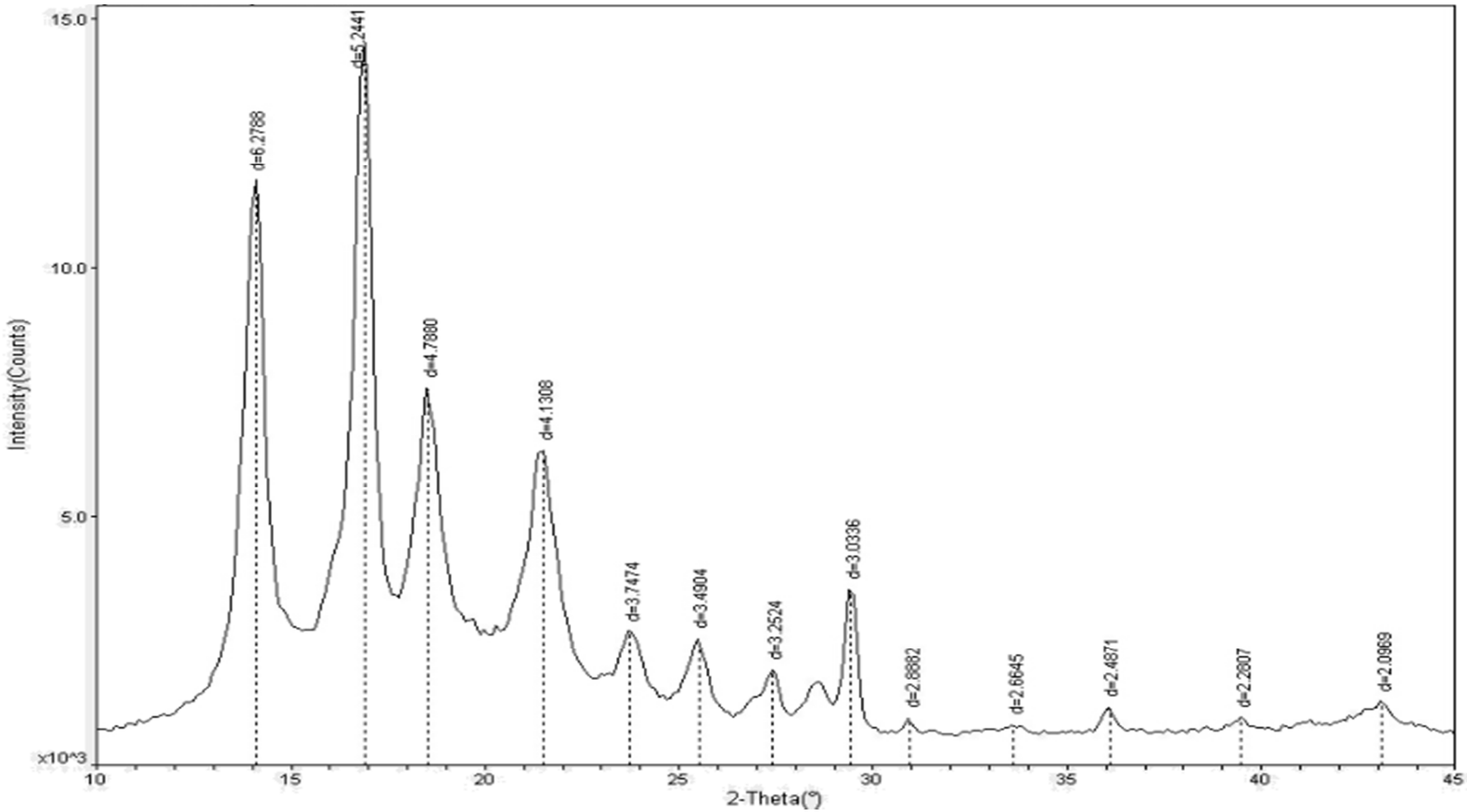

Figure A.1.3 : XRD diagram of RPP/5%EPDM/HPN 68L/I-168

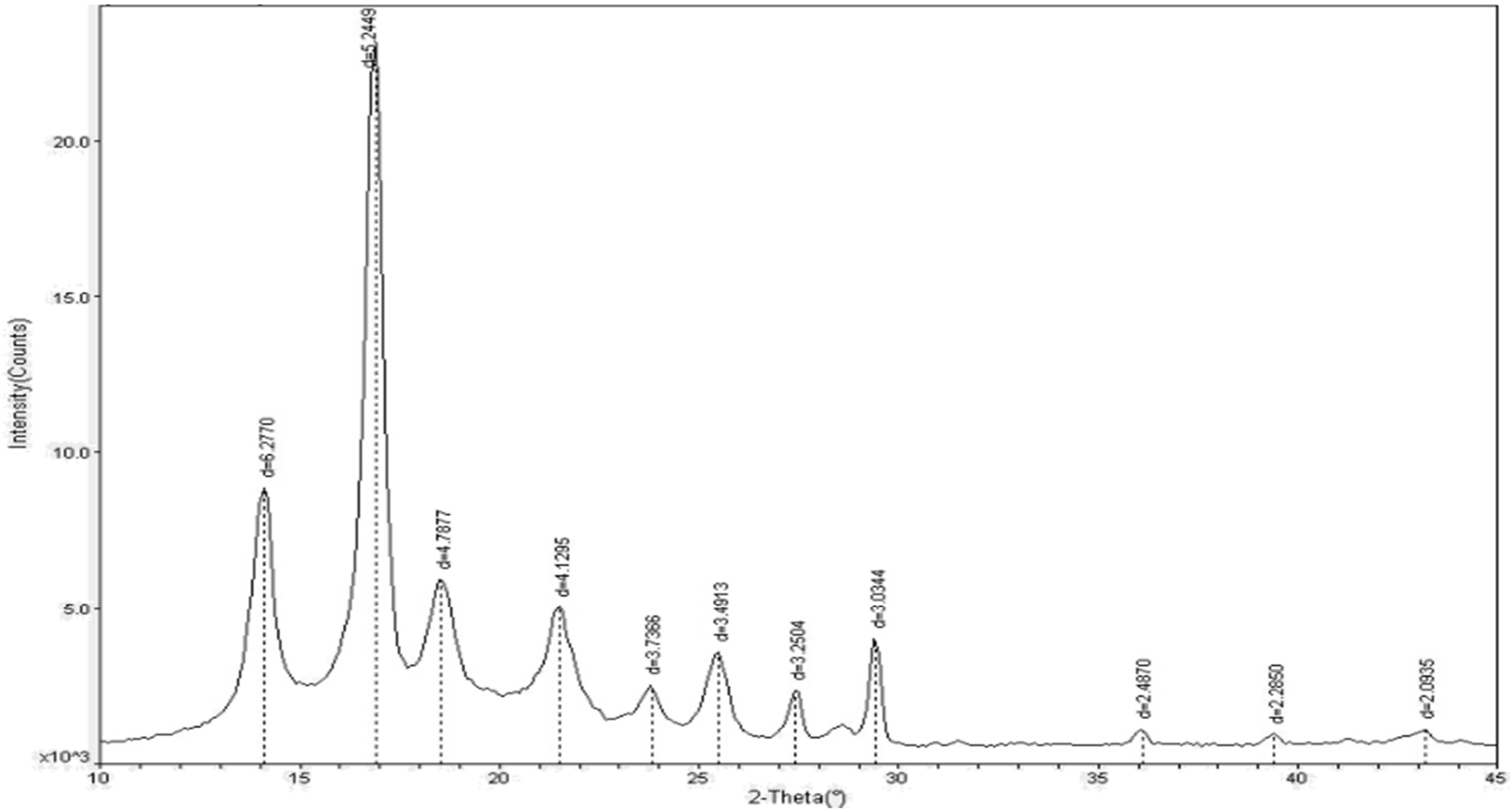

Figure A.1.4 : XRD diagram of RPP/5%EPDM/HPN 20E/I-168

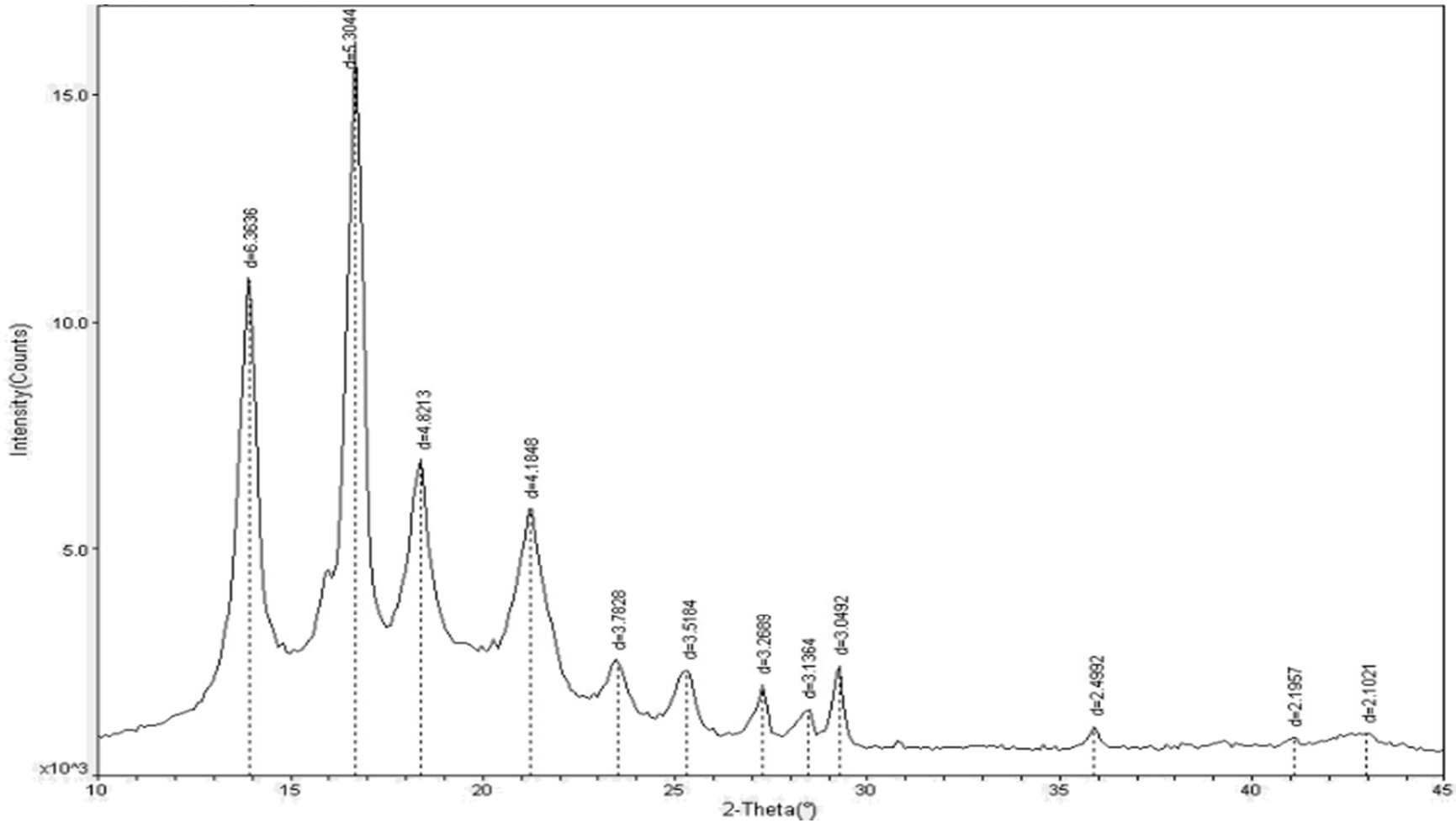

Figure A.1.5 : XRD diagram of RPP/10%EPDM/NA-11UH/I-168

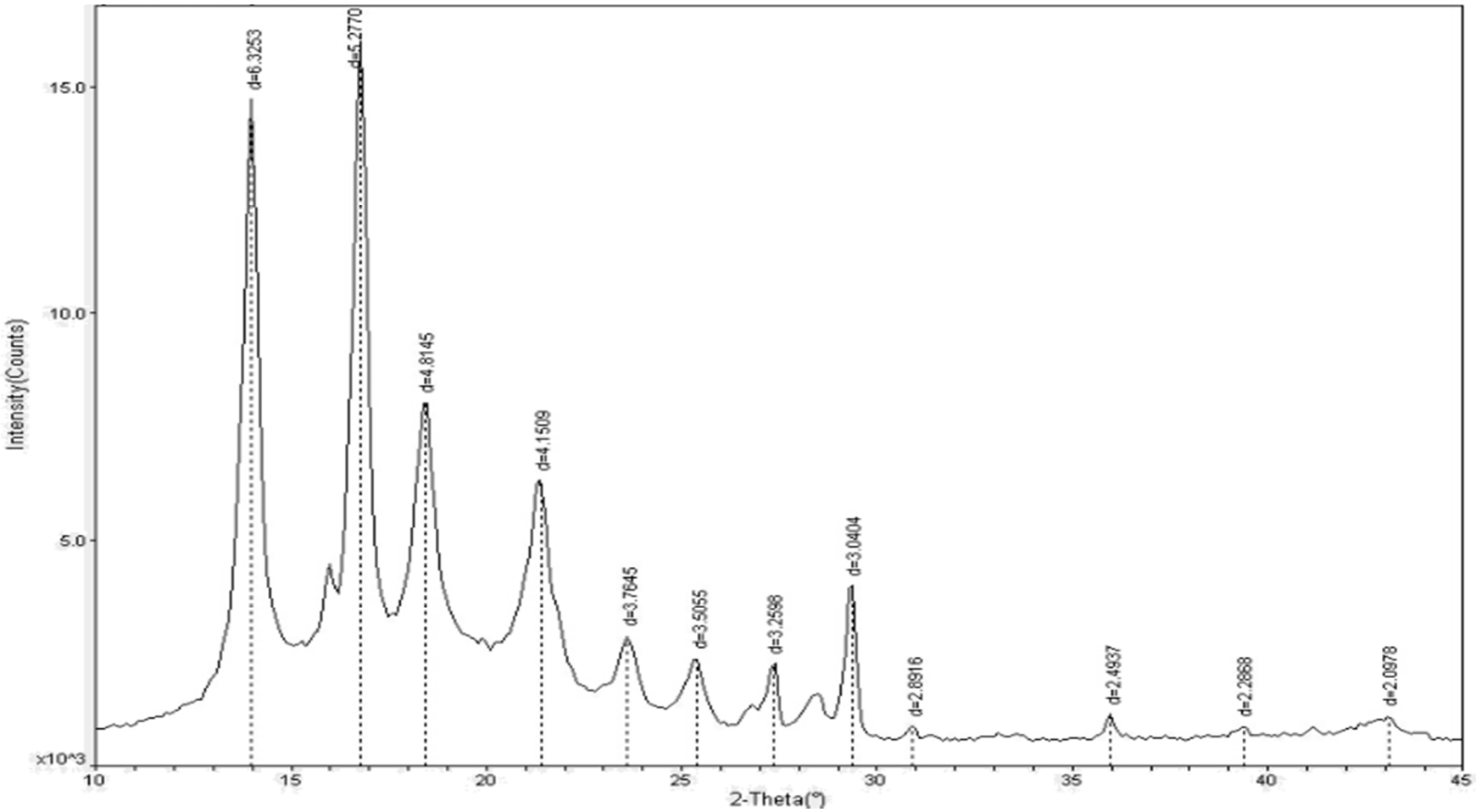

Figure A.1.6 : XRD diagram of RPP/10%EPDM/HPN 68L/I-168

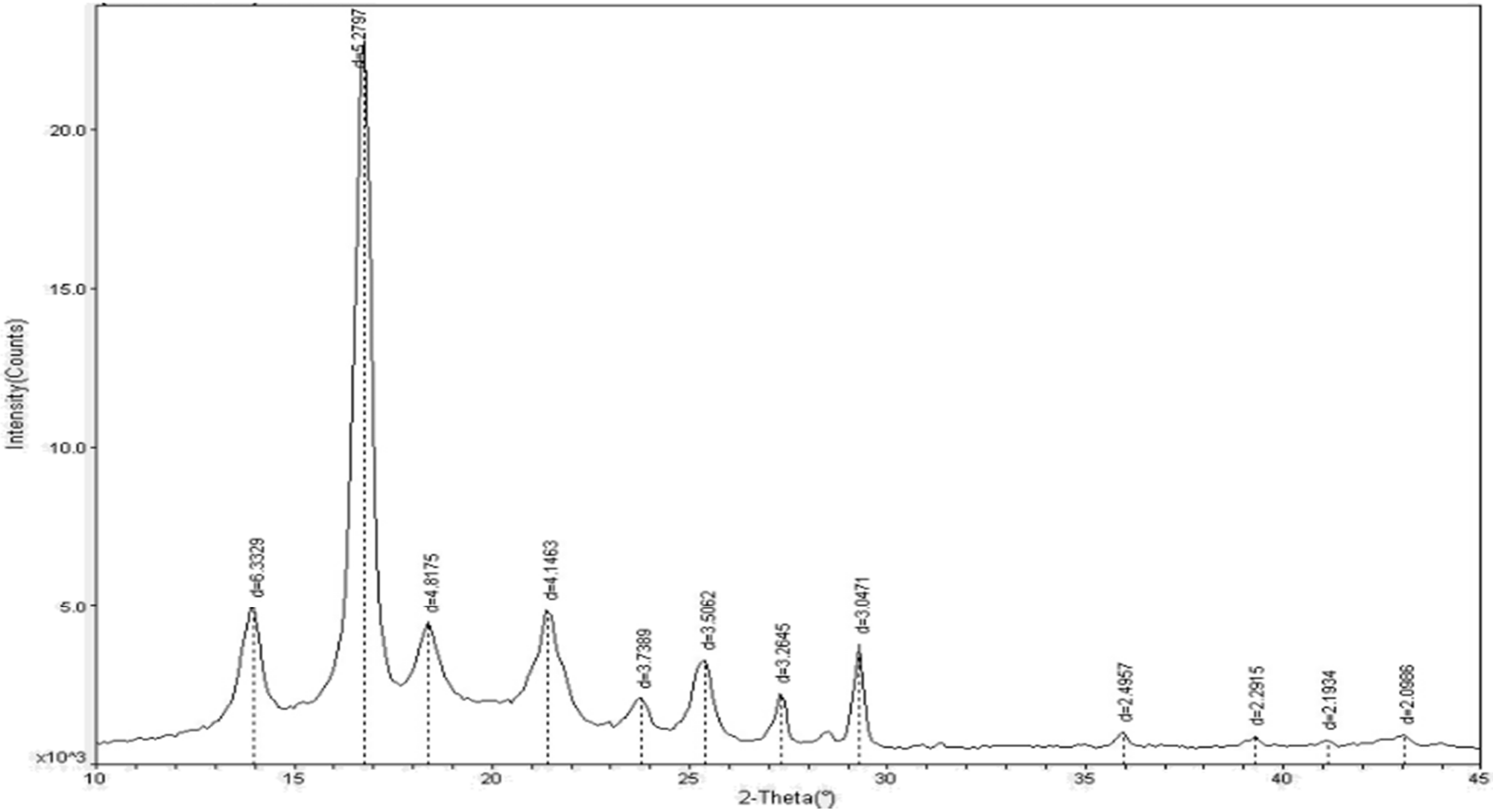

Figure A.1.7 : XRD diagram of RPP/10%EPDM/HPN 20E/I-168

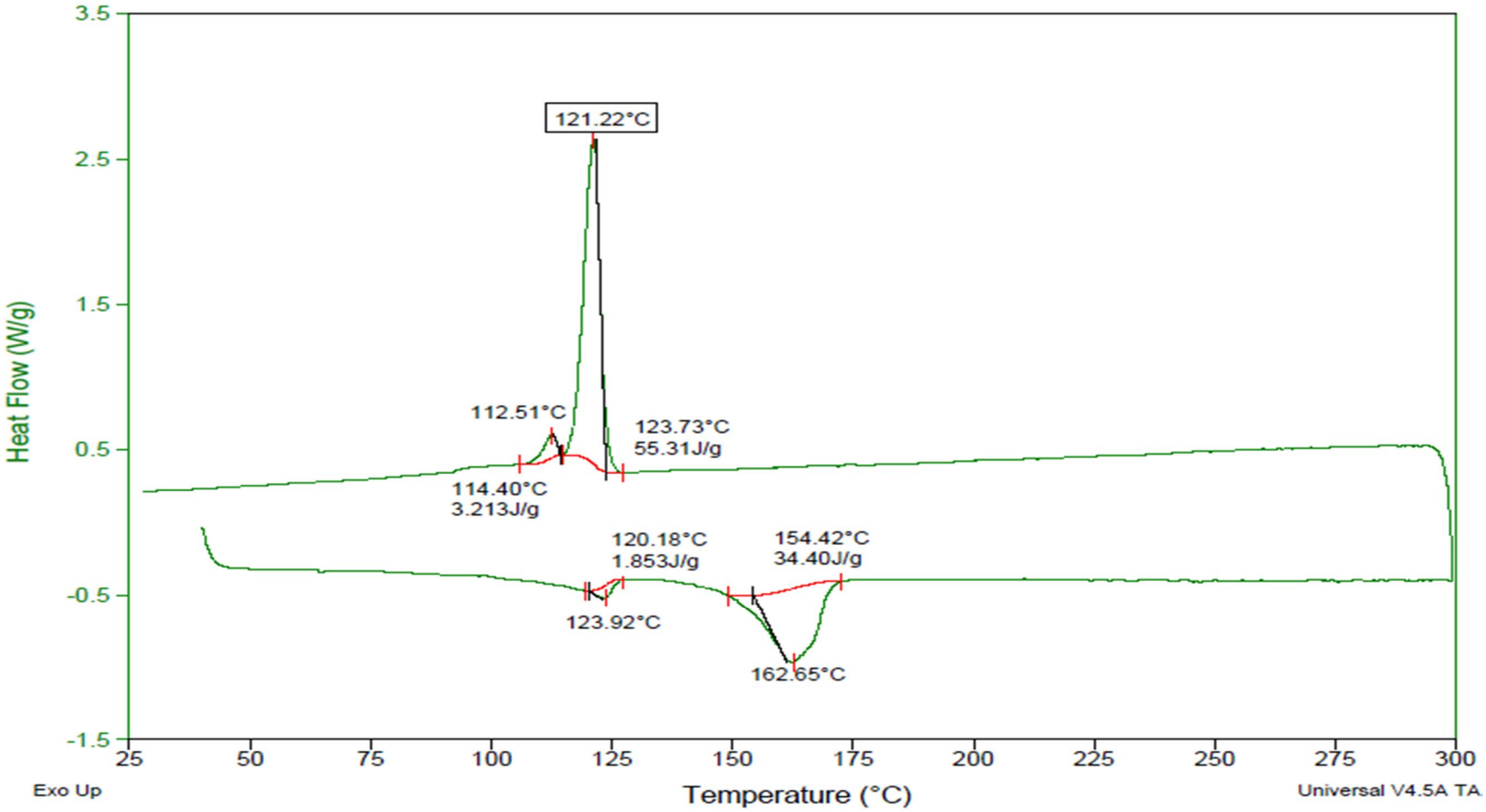

Figure A.2.1 : DSC diagram of RPP

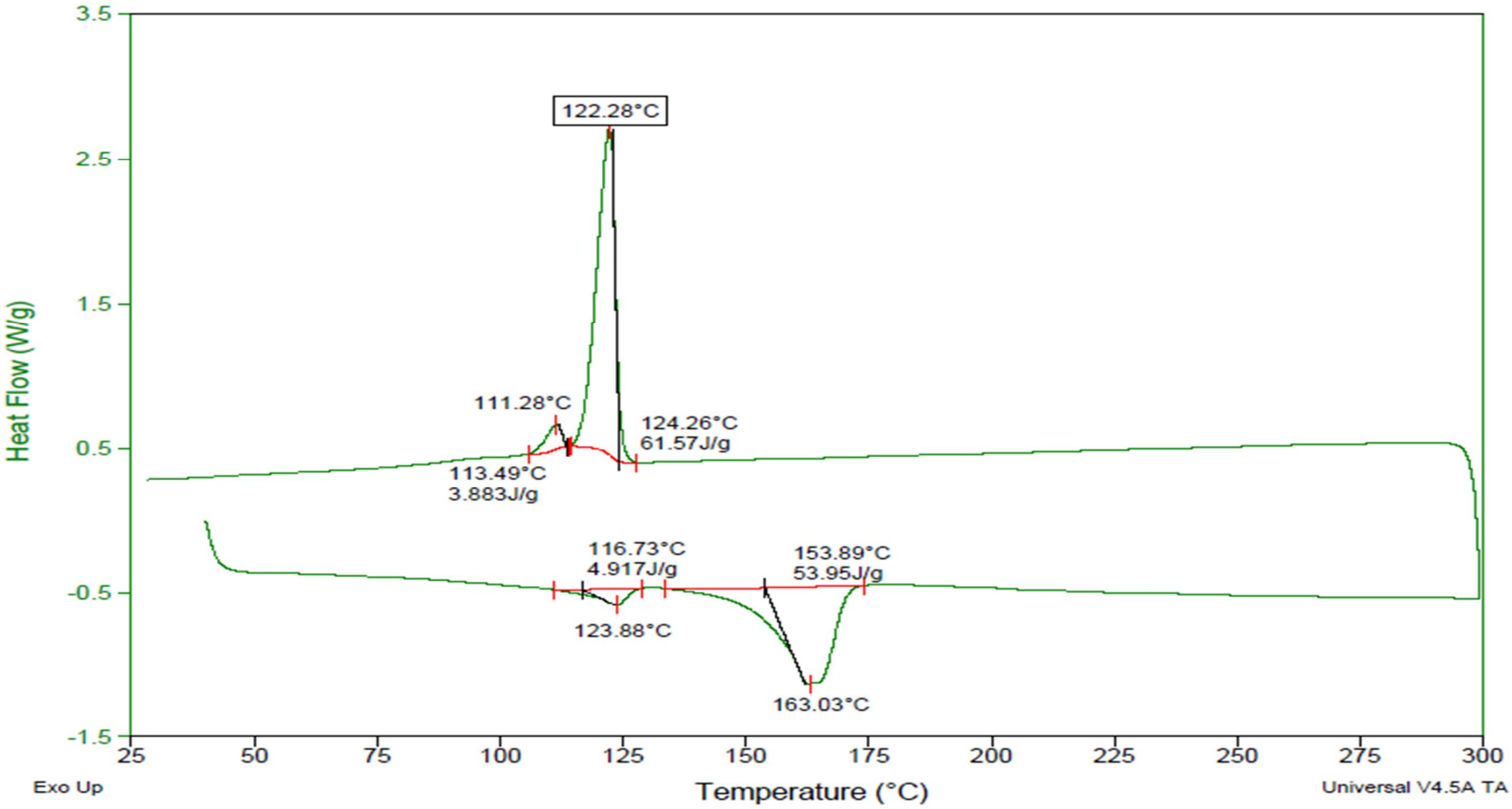

Figure A.2.2 : DSC diagram of RPP/5% 3092 PM mono mixture

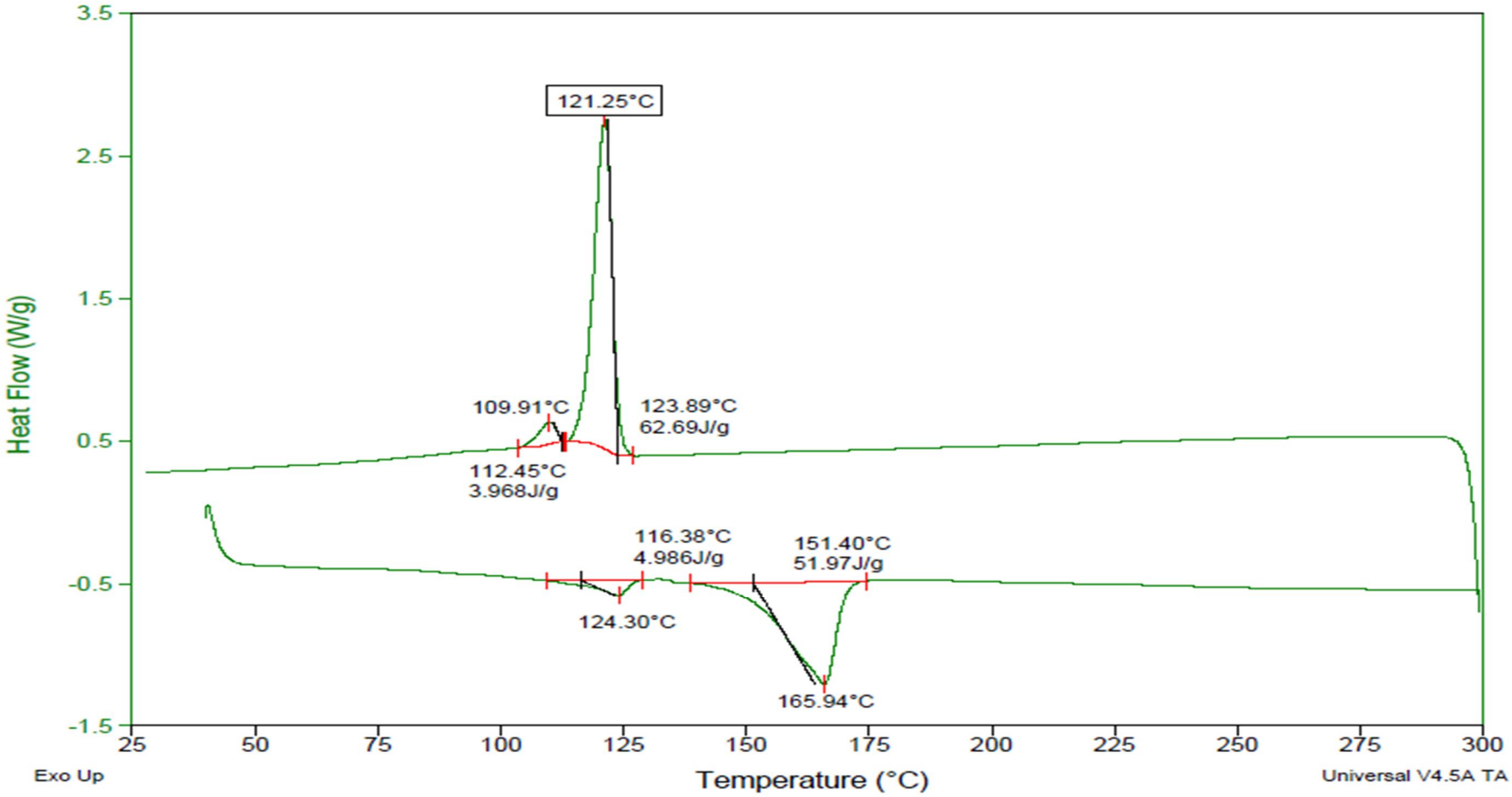

Figure A.2.3 : DSC diagram of RPP/10% 3092 PM mono mixture

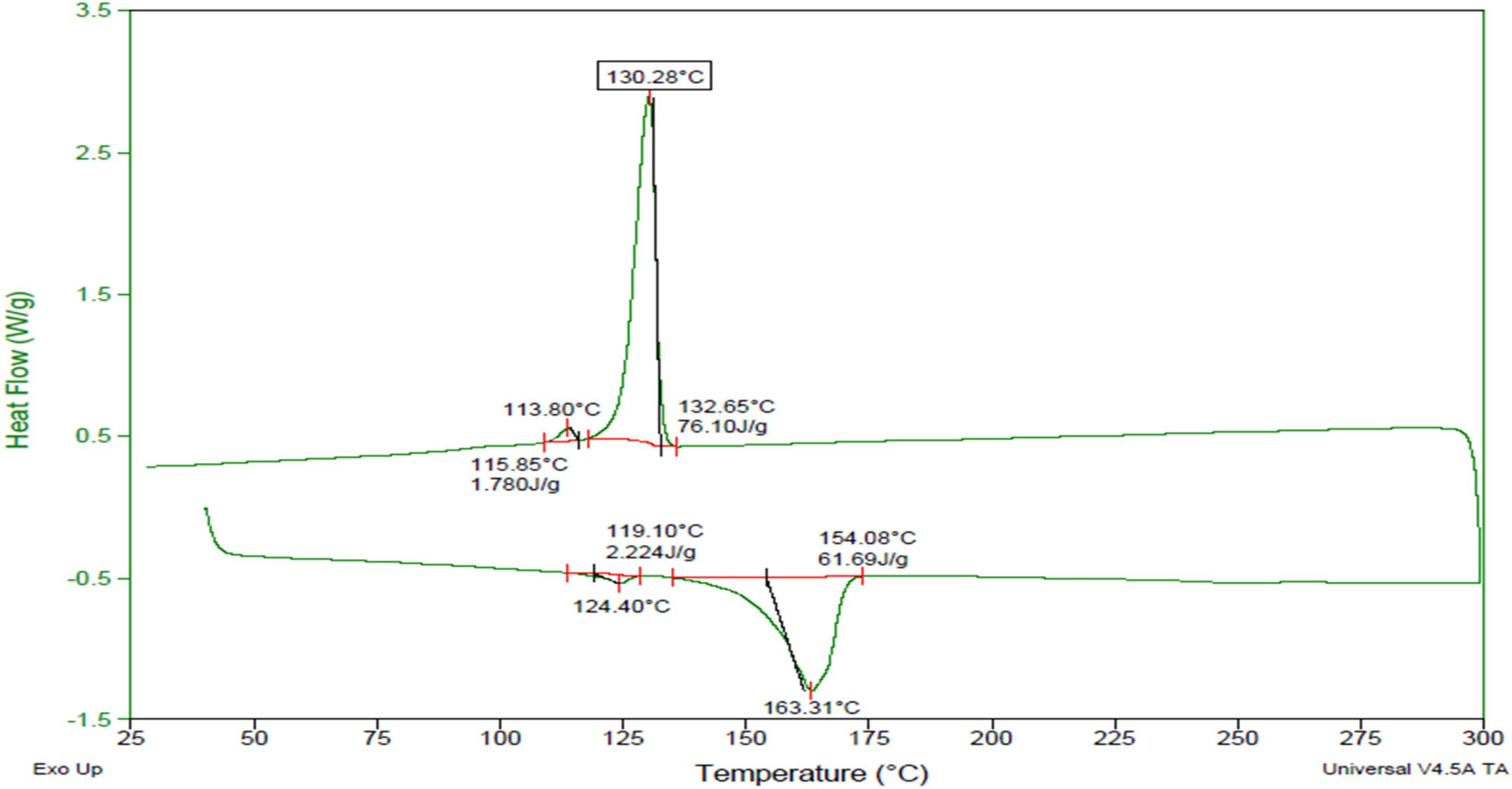

Figure A.2.4 : DSC diagram of RPP/NA-11UH mono mixture

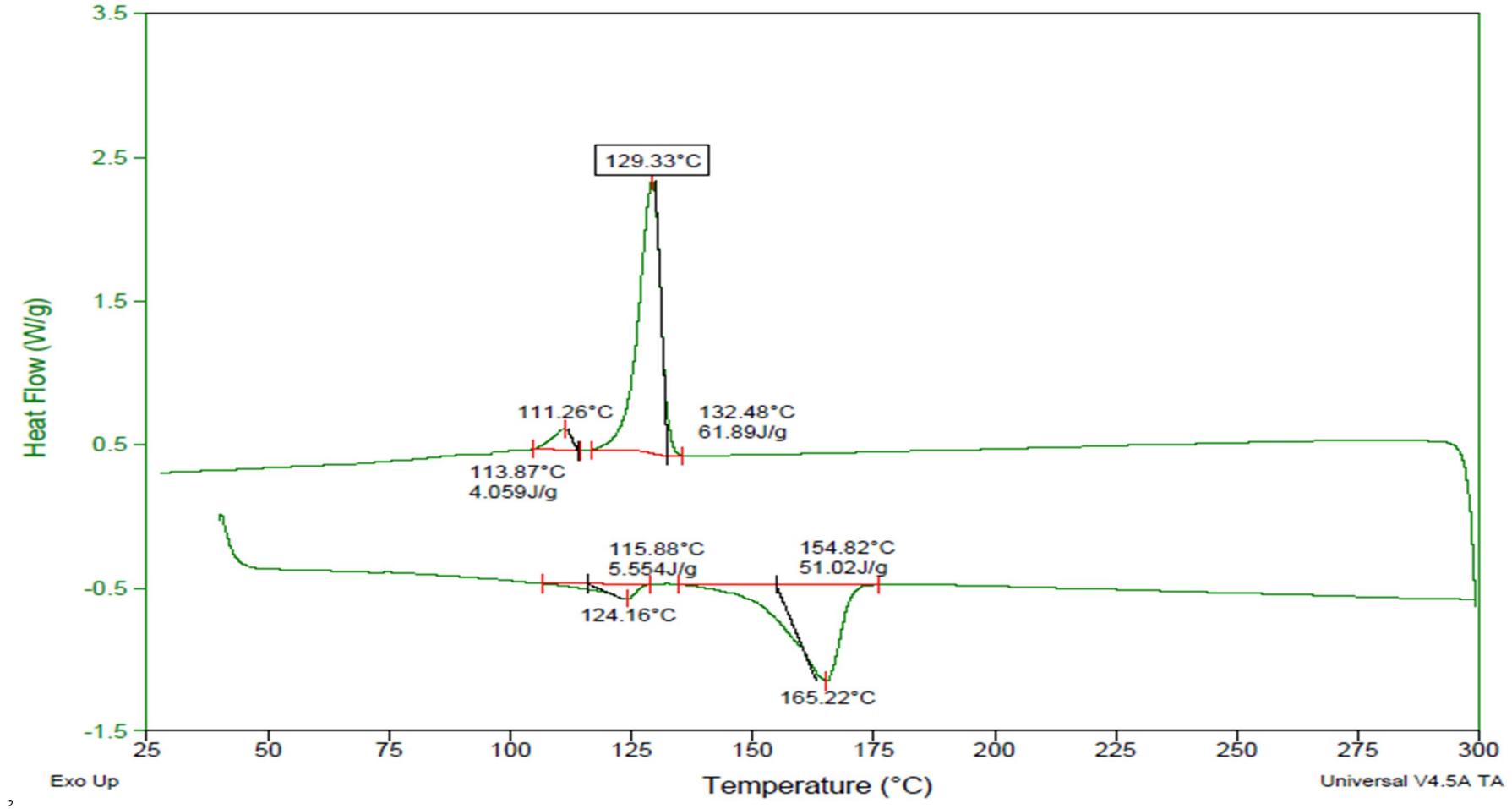

Figure A.2.5 : DSC diagram of RPP/HPN 68L mono mixture

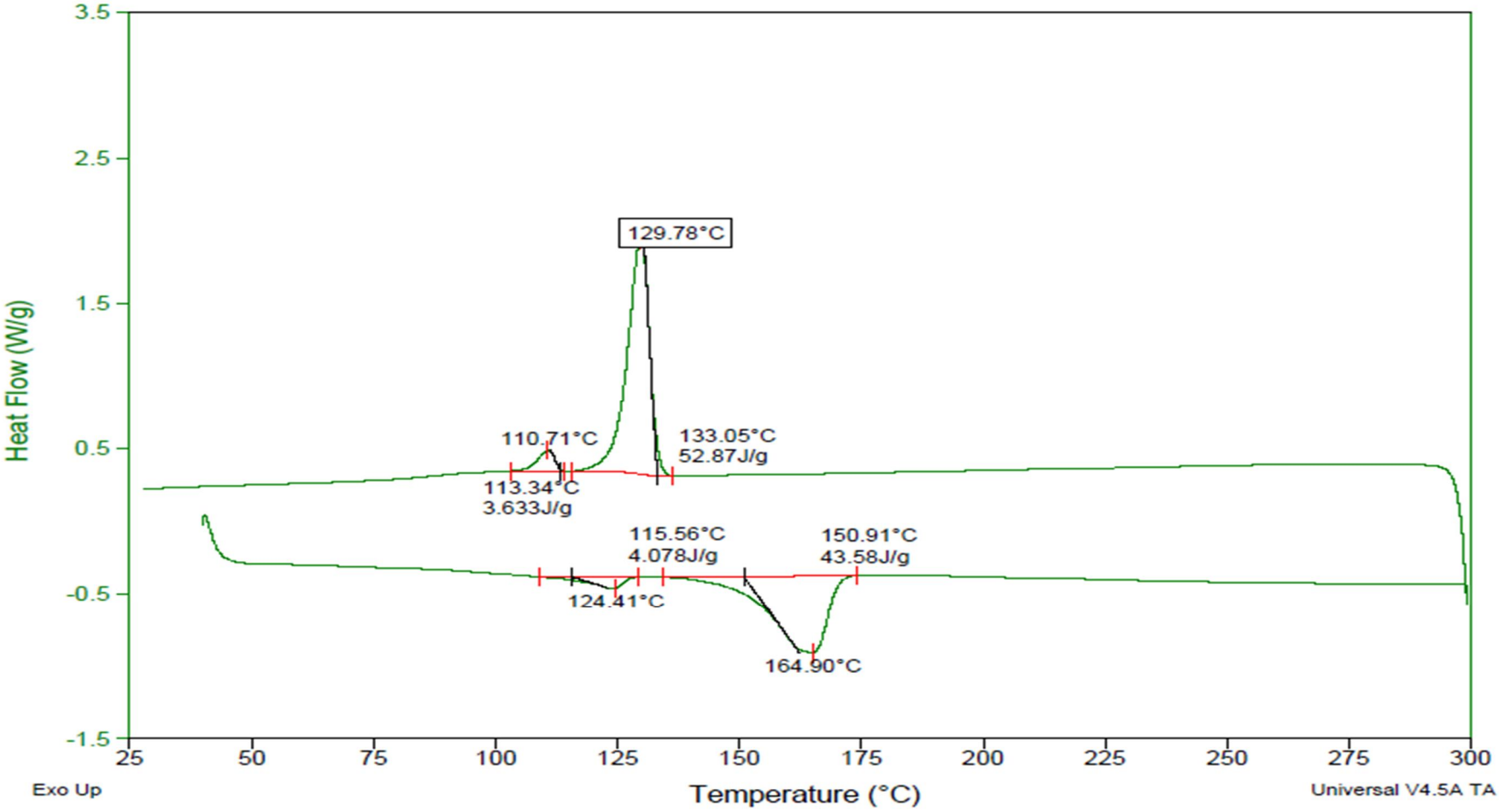

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Figure A.2.6 : DSC diagram of RPP/HPN 20E mono mixture

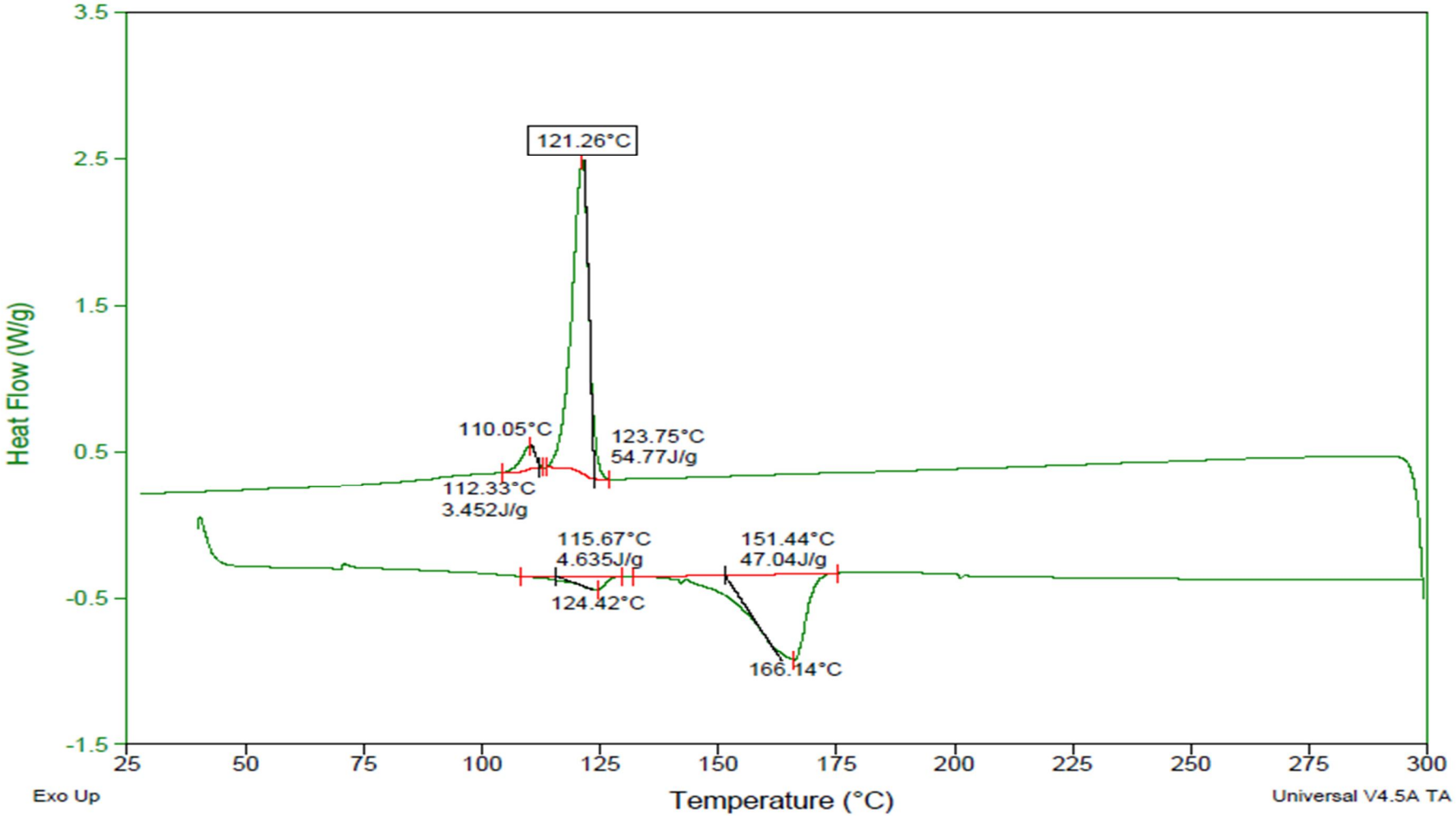

Figure A.2.7 : DSC diagram of RPP/I-168 mono mixture

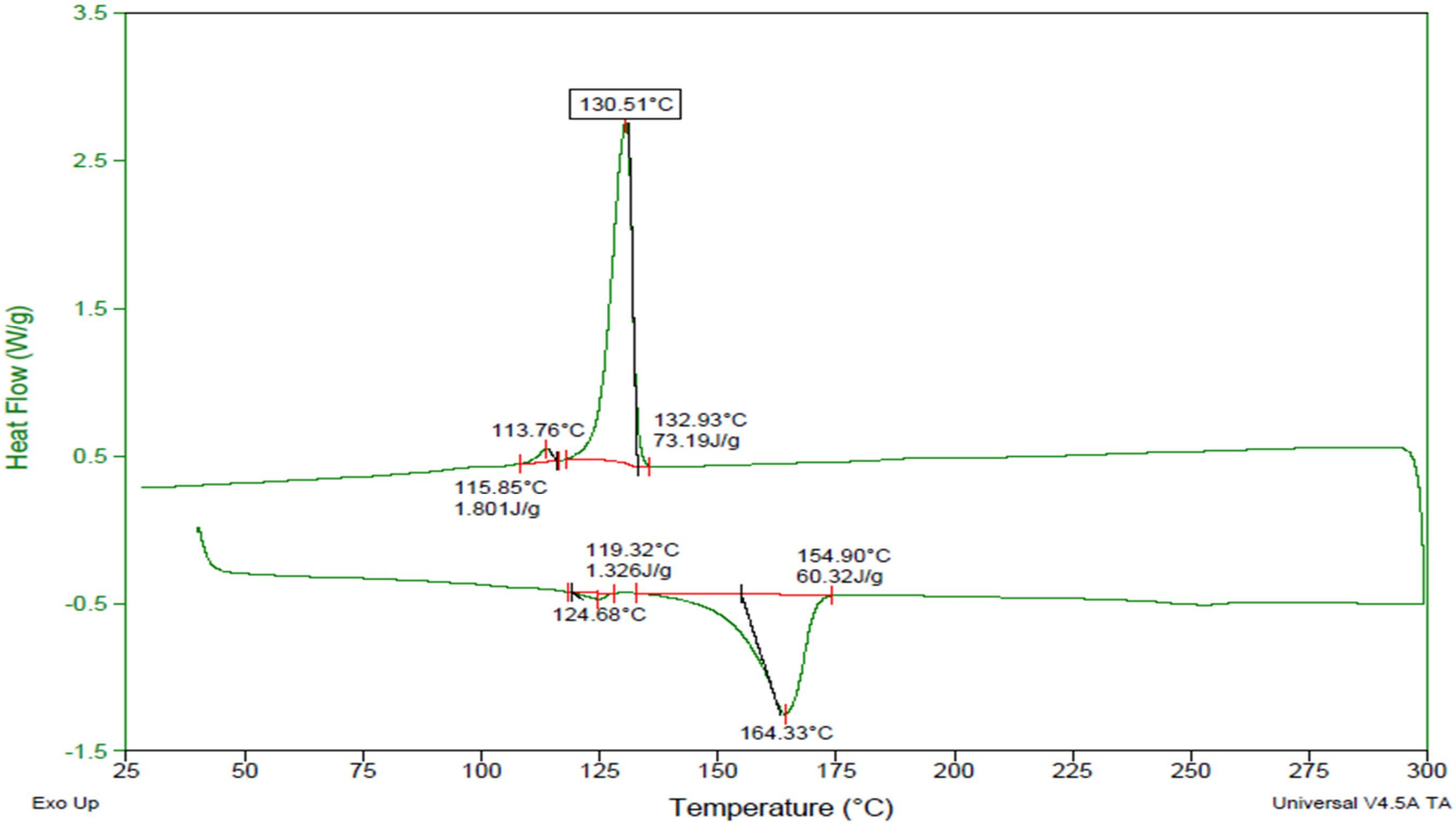

Figure A.2.8 : DSC diagram of RPP/NA-11UH/I-168 binary mixture

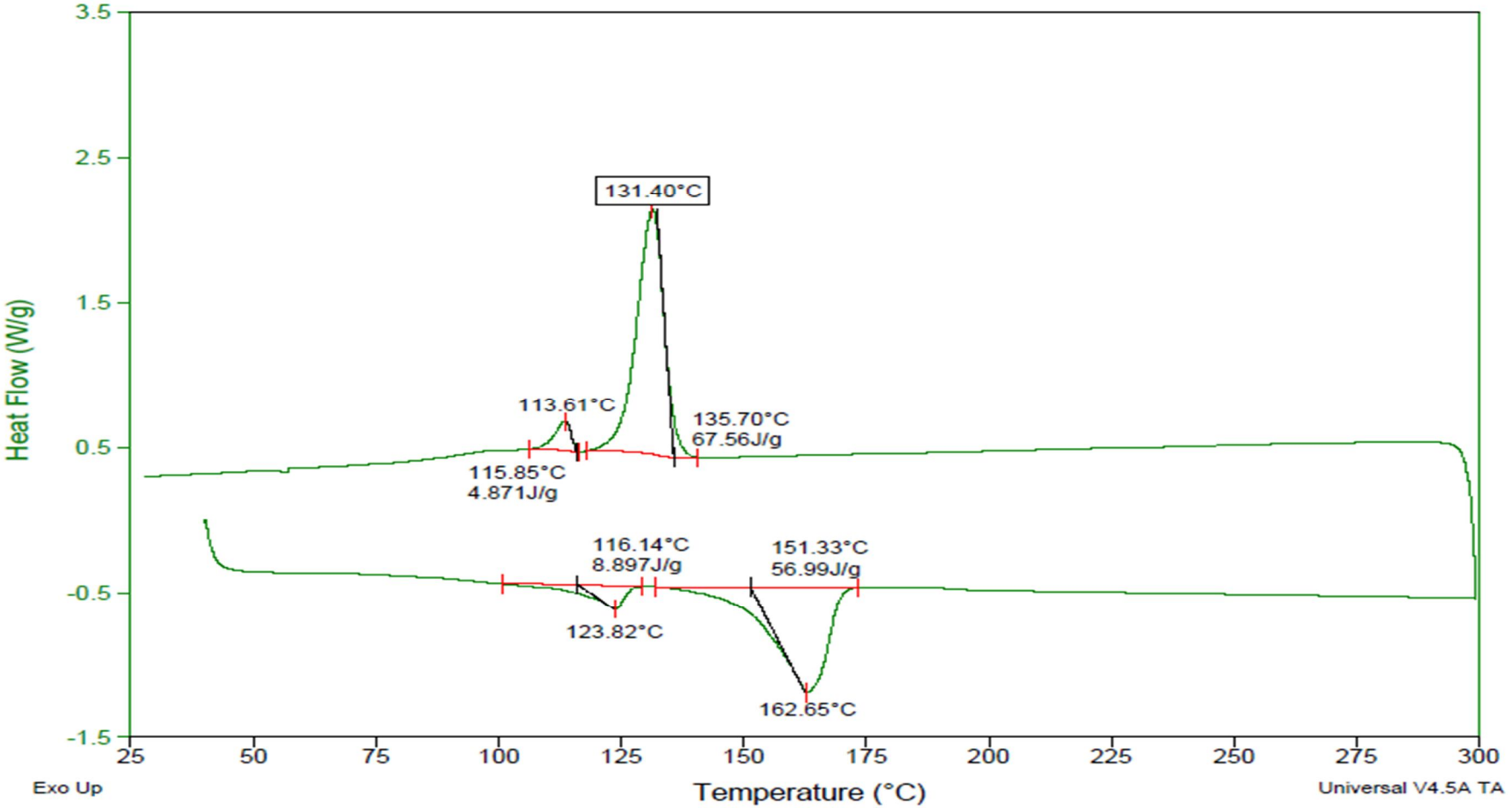

Figure A.2.9 : DSC diagram of RPP/HPN 68L/I-168 binary mixture

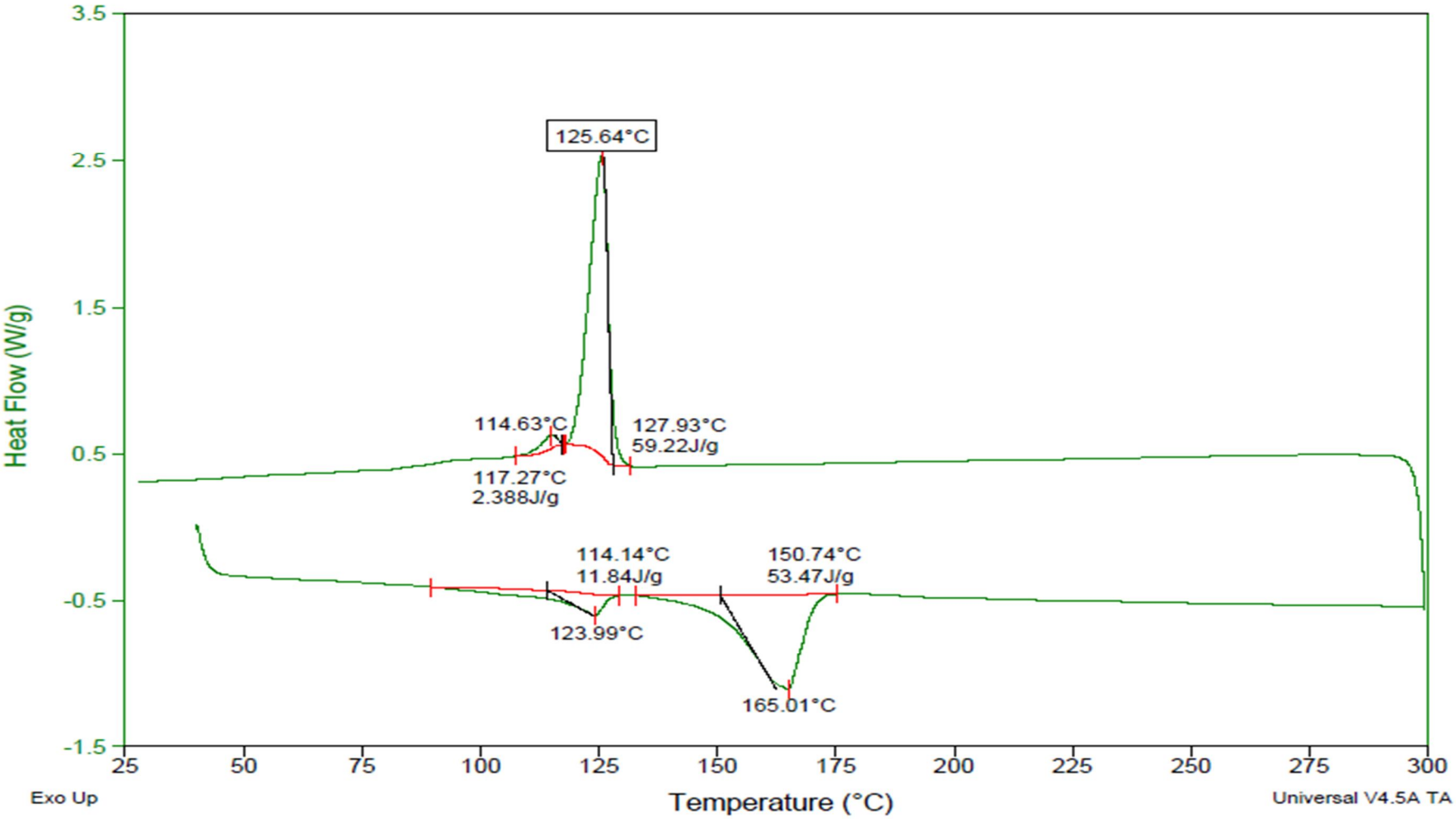

Figure A.2.10 : DSC diagram of RPP/HPN 20E/I-168 binary mixture

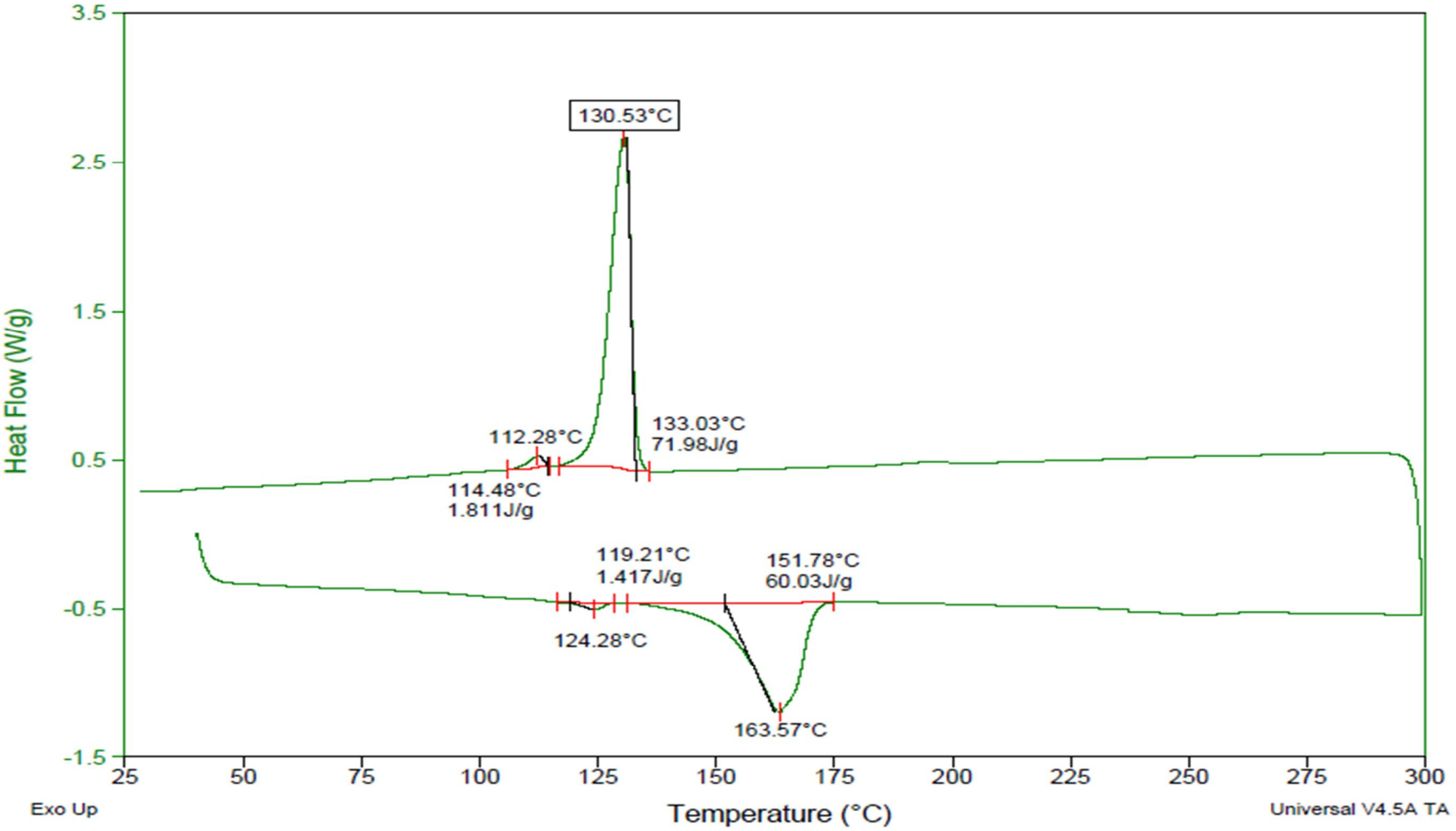

Figure A.2.11 : DSC diagram of RPP/5% EPDM/NA-11UH binary mixture

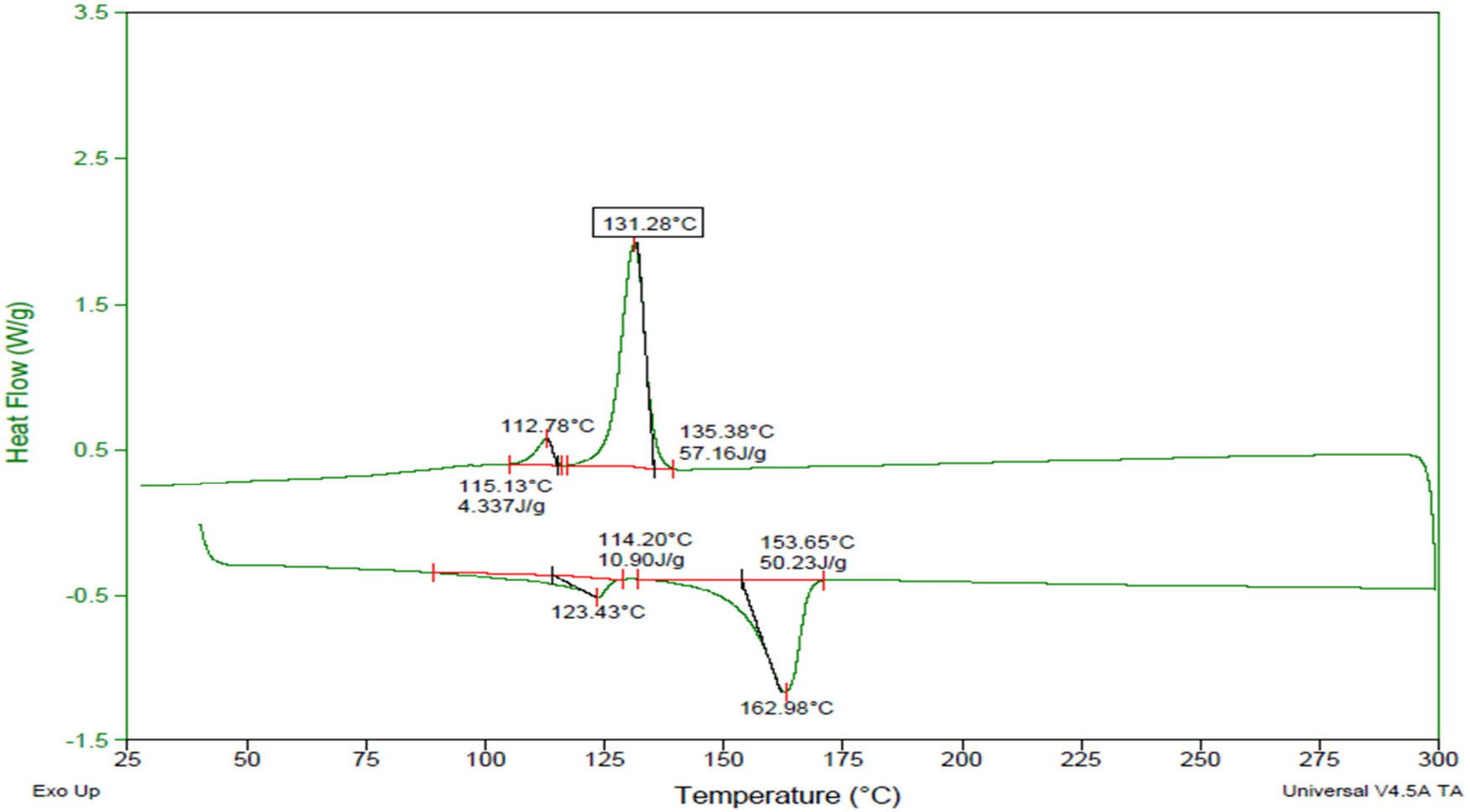

Figure A.2.12 : DSC diagram of RPP/5% EPDM/HPN 68L binary mixture

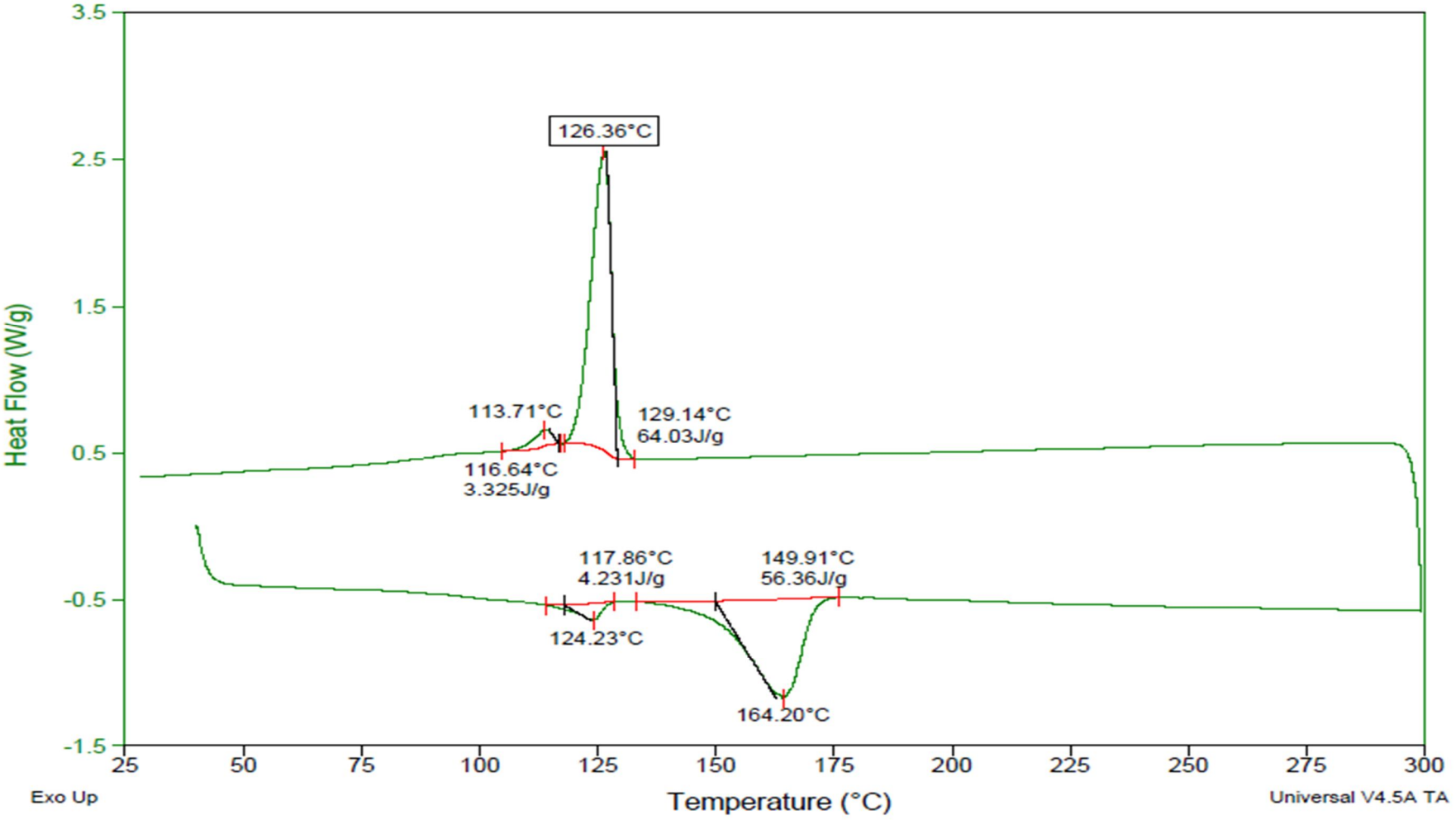

Figure A.2.13 : DSC diagram of RPP/5% EPDM/HPN 20E binary mixture

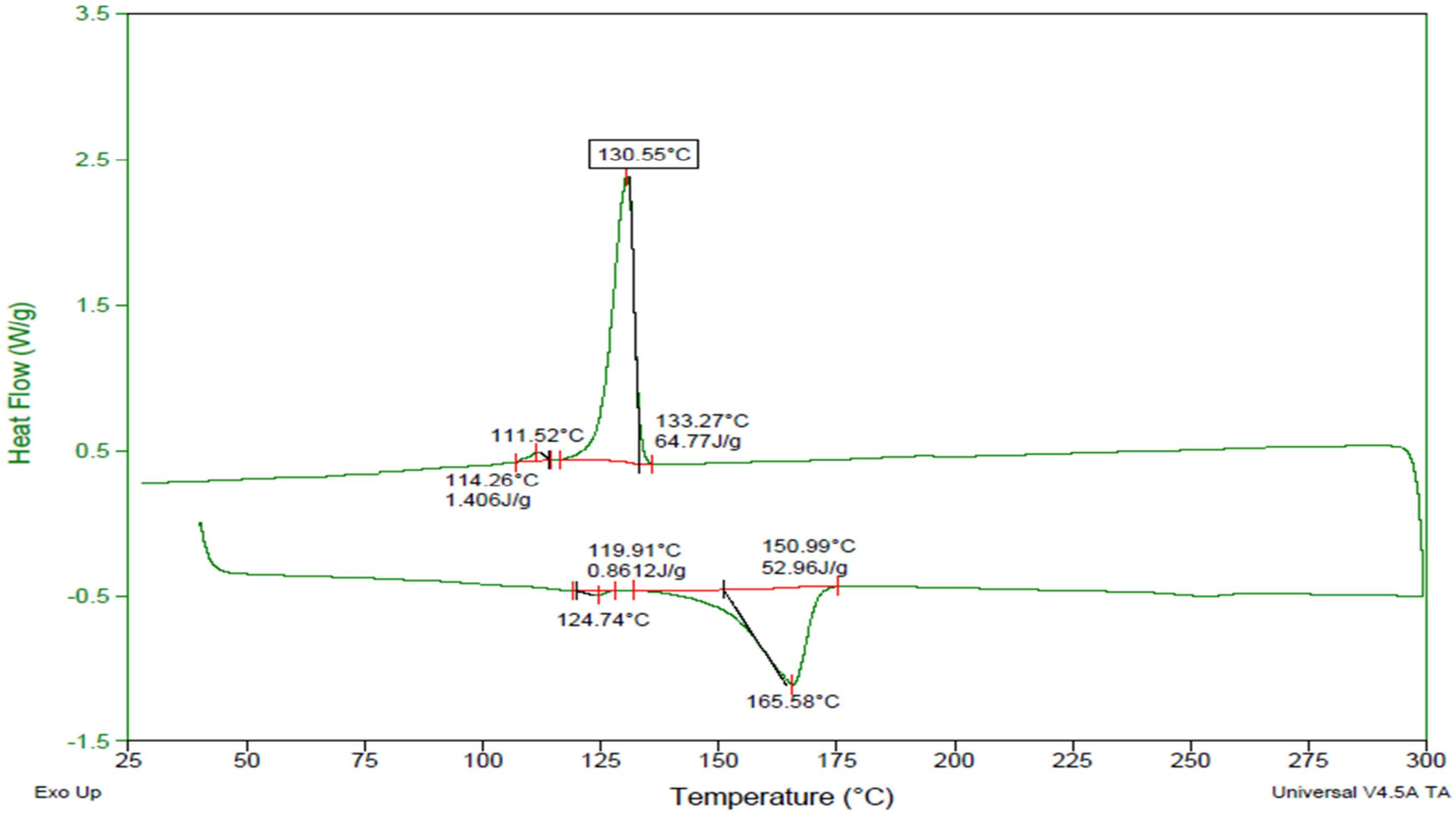

Figure A.2.14 : DSC diagram of RPP/10% EPDM/NA-11UH binary mixture

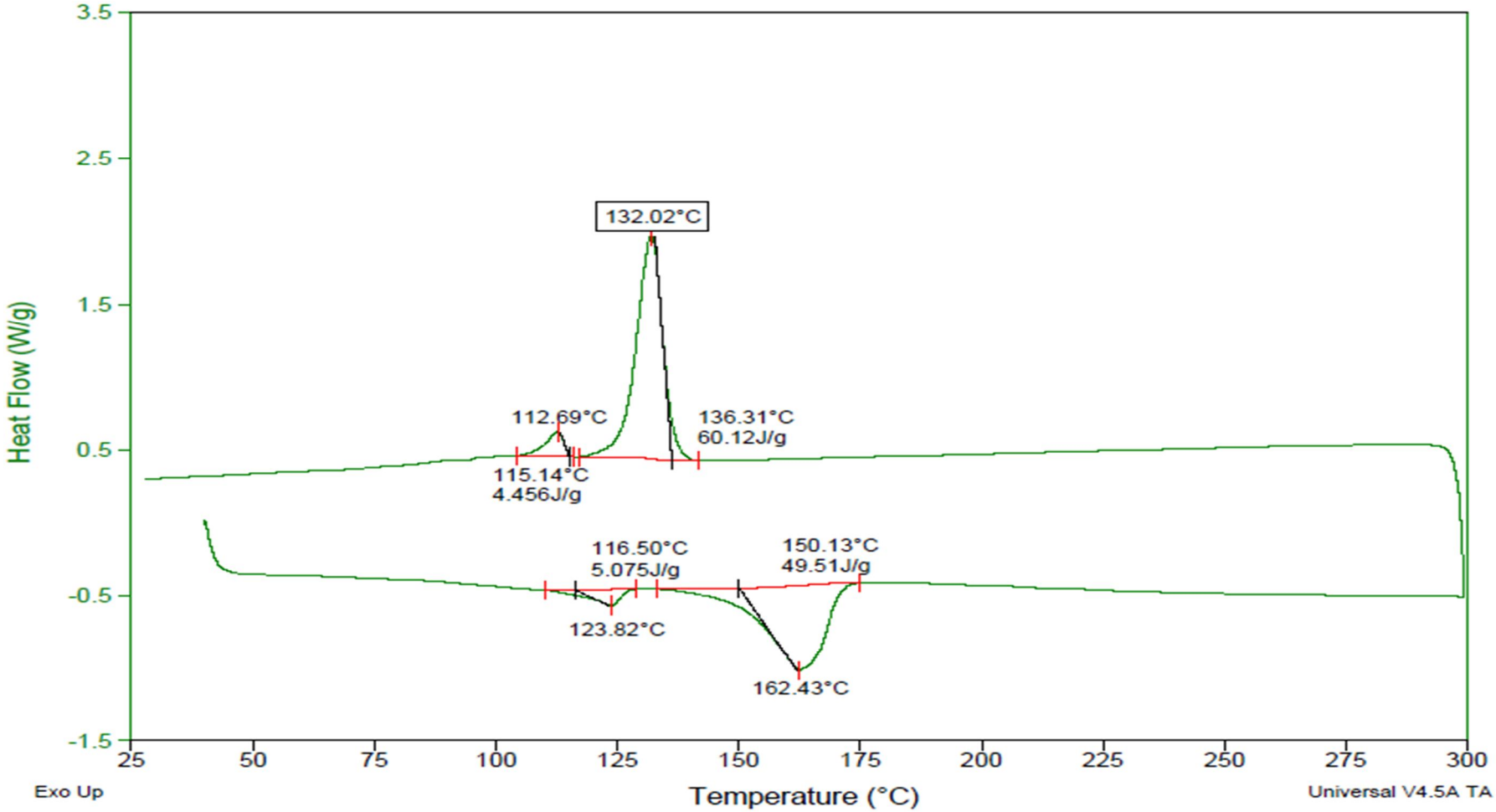

Figure A.2.15 : DSC diagram of RPP/10% EPDM/HPN 68L binary mixture

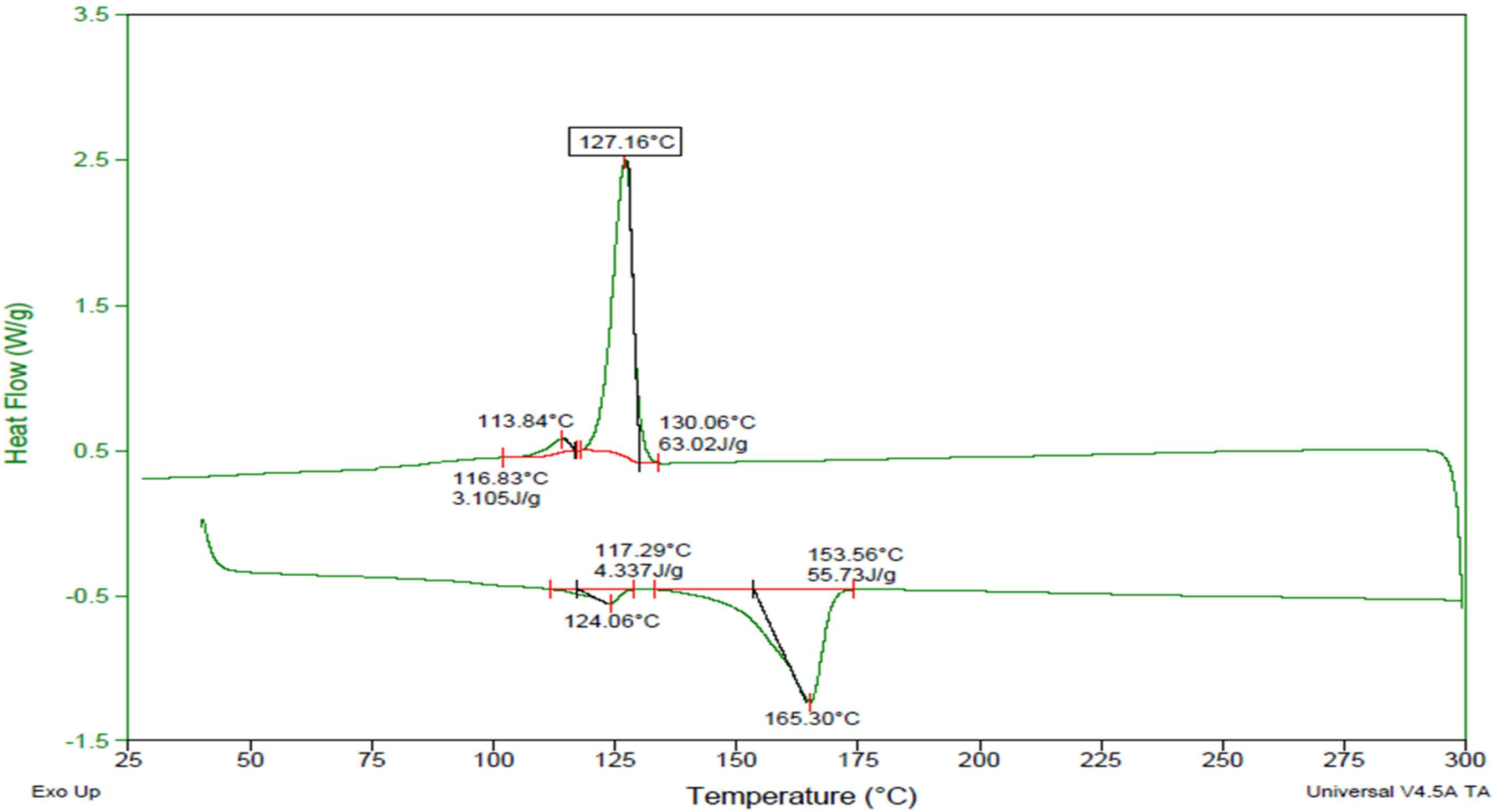

Figure A.2.16 : DSC diagram of RPP/10% EPDM/HPN 20E binary mixture

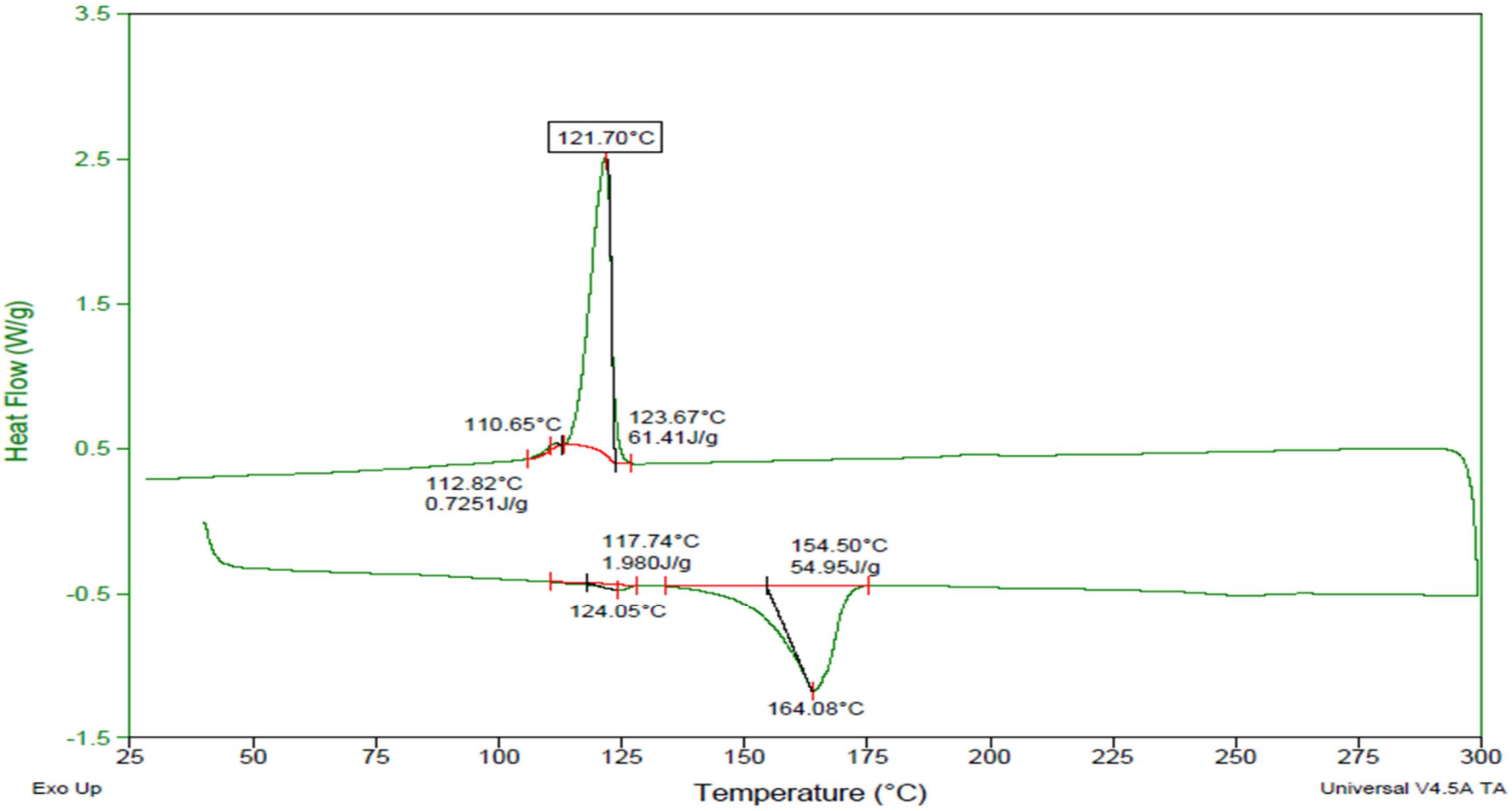

Figure A.2.17 : DSC diagram of RPP/5% EPDM/I-168 binary mixture

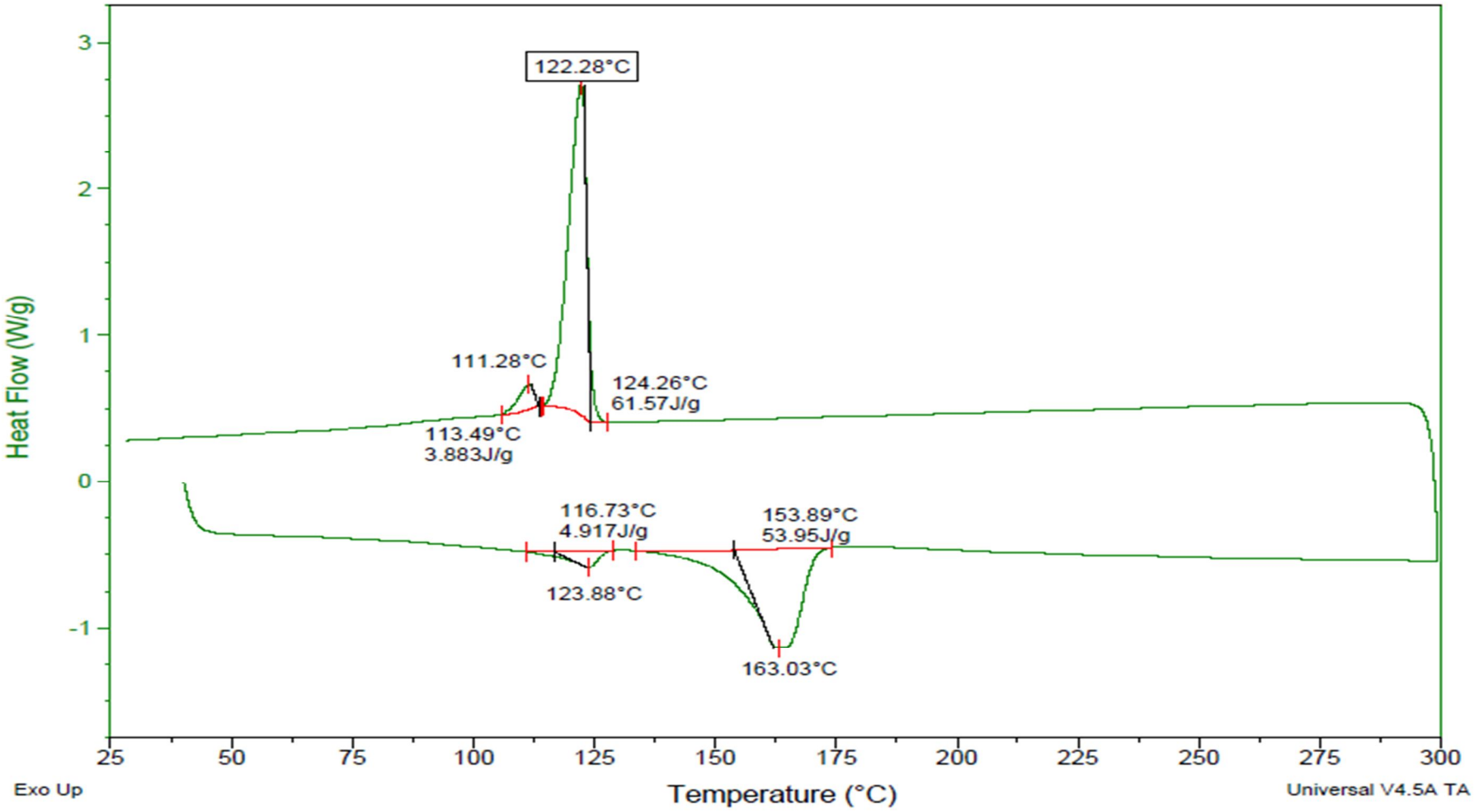

Figure A.2.18 : DSC diagram of RPP/10% EPDM/I-168 binary mixture

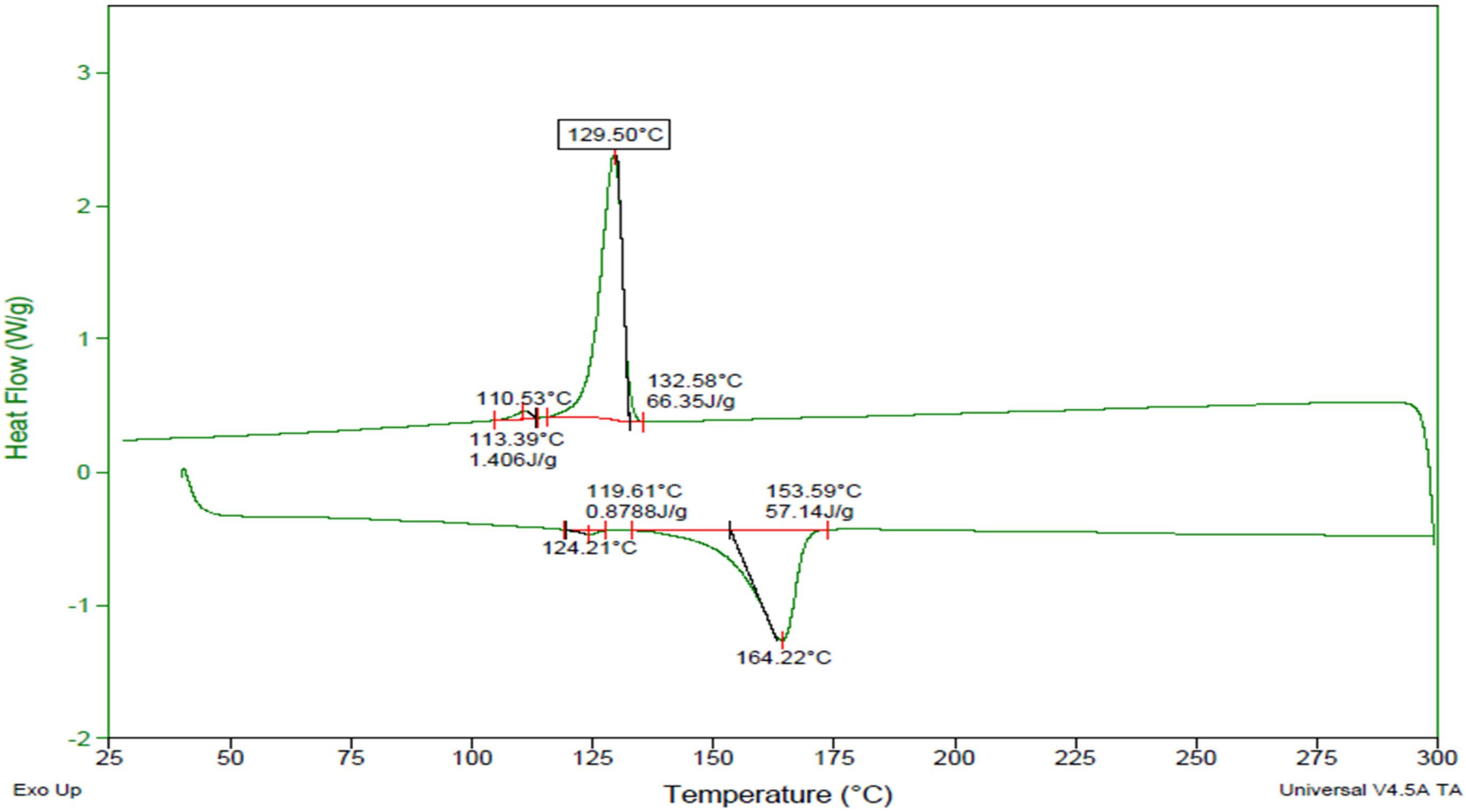

Figure A.2.19 : DSC diagram of RPP/5% EPDM/NA-11UH/I-168 ternary mixture

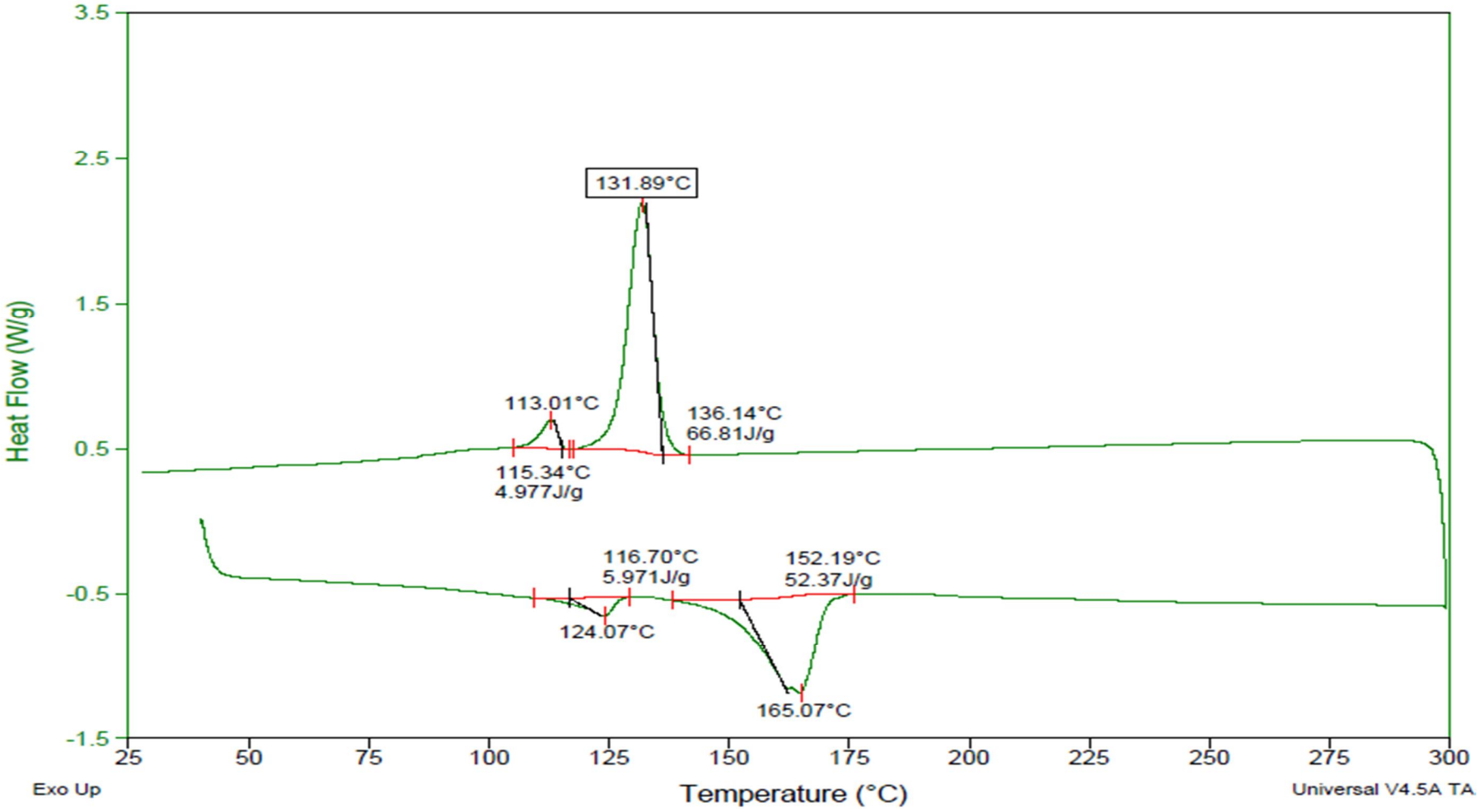

Figure A.2.20 : DSC diagram of RPP/5% EPDM/HPN 68L/I-168 ternary mixture

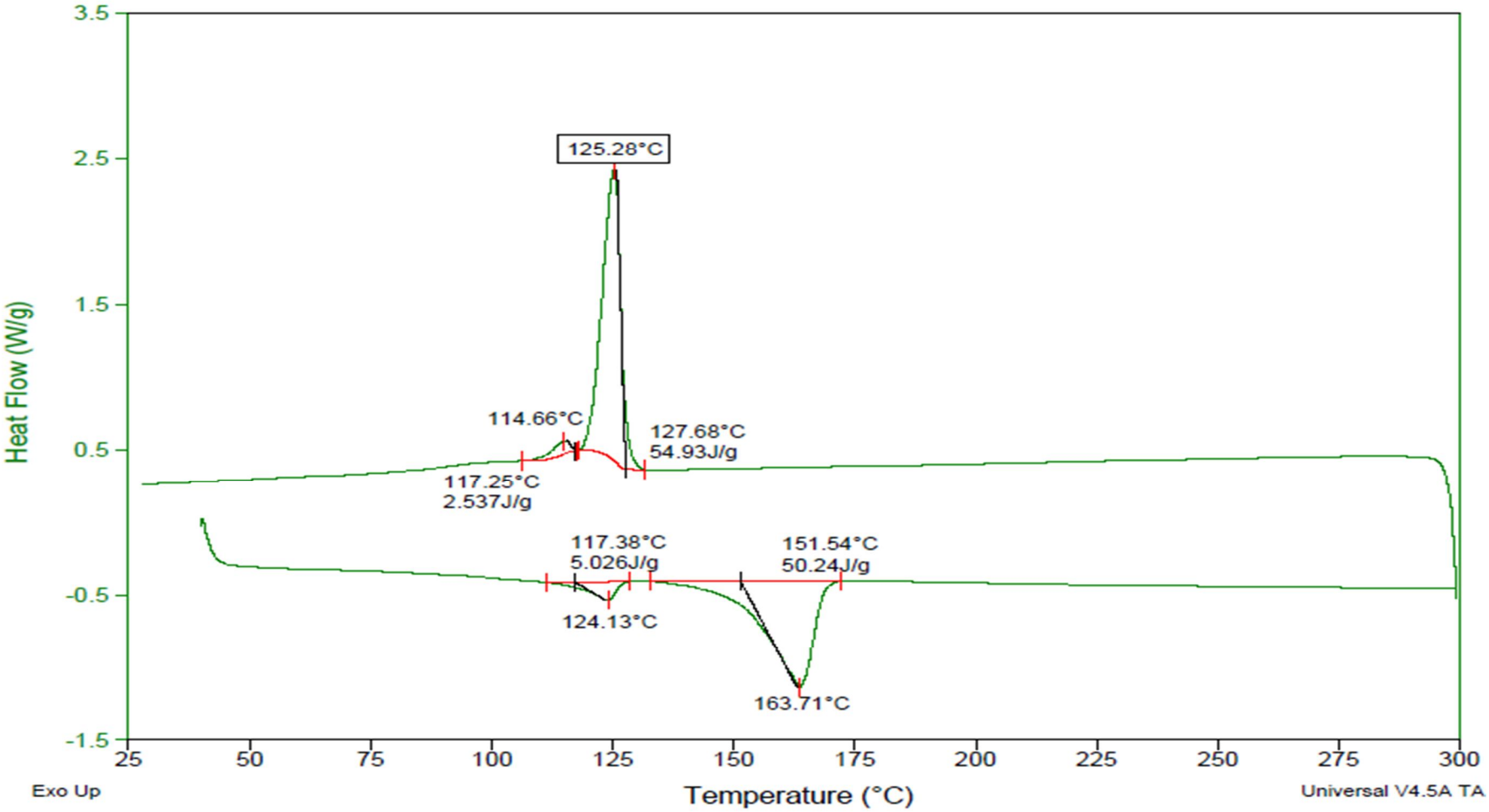

Figure A.2.21 : DSC diagram of RPP/5% EPDM/HPN 20E/I-168 ternary mixture

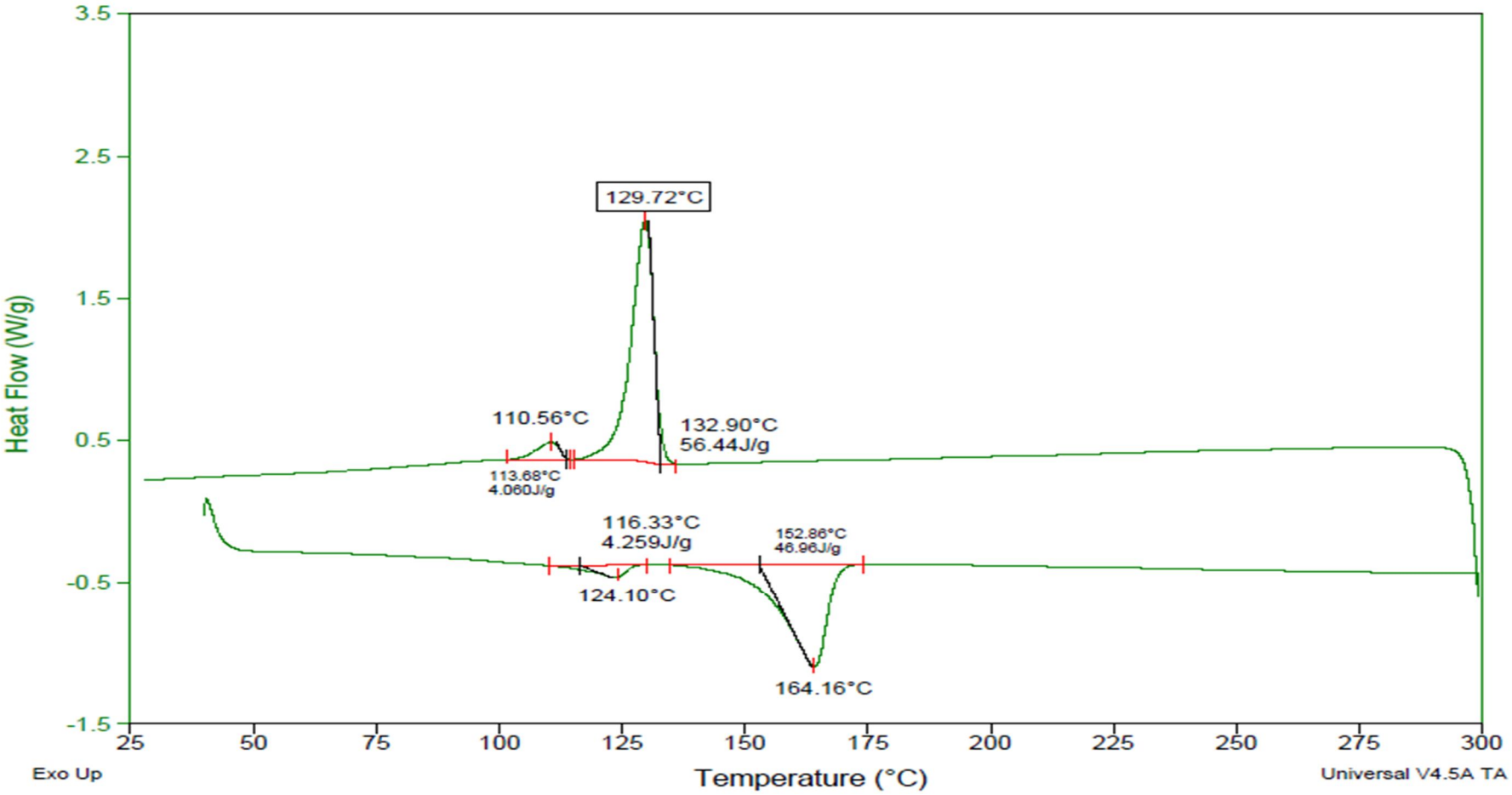

Figure A.2.22 : DSC diagram of RPP/10% EPDM/NA-11UH/I-168 ternary mixture

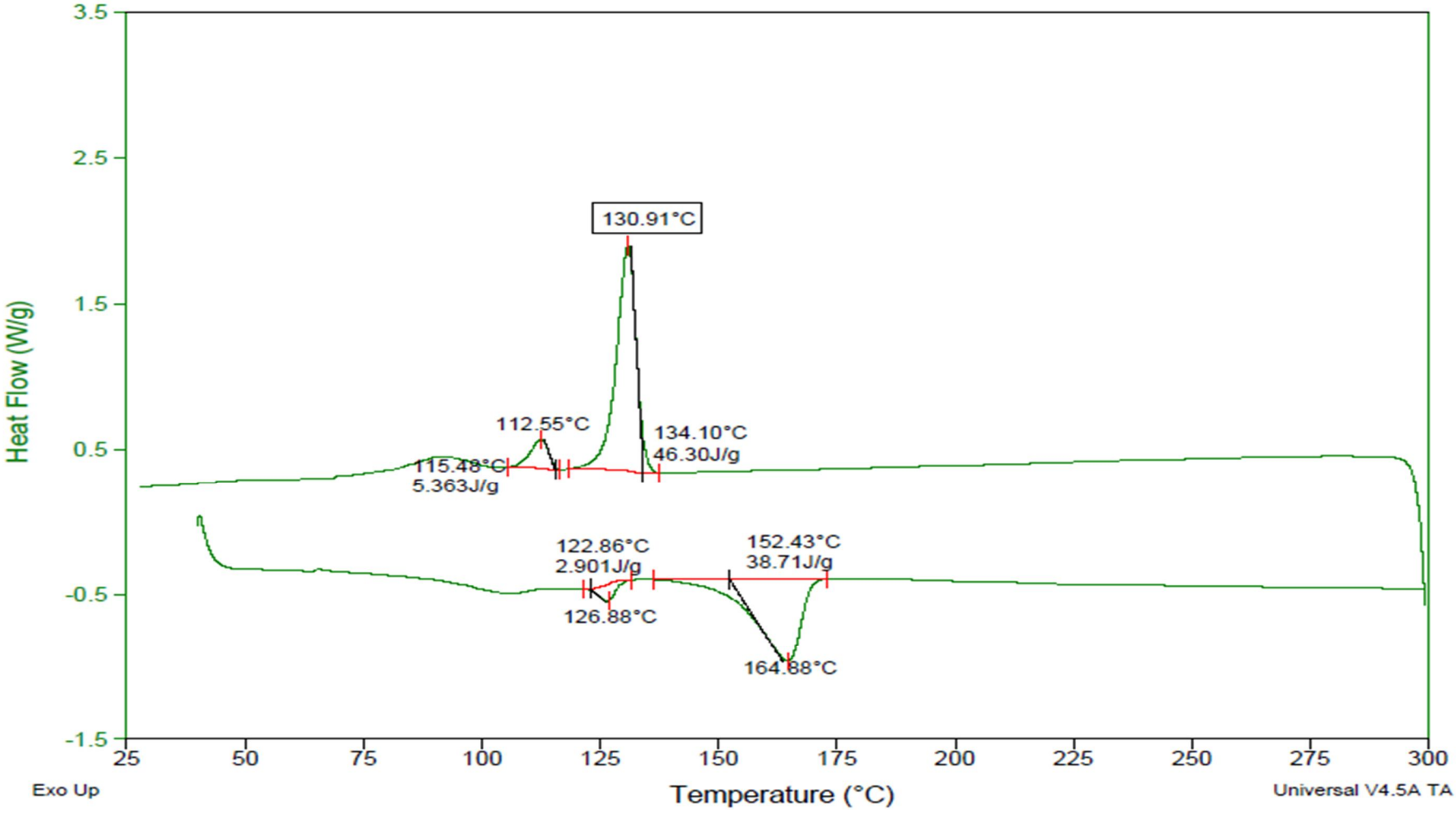

Figure A.2.23 : DSC diagram of RPP/10% EPDM/HPN 68L/I-168 ternary mixture

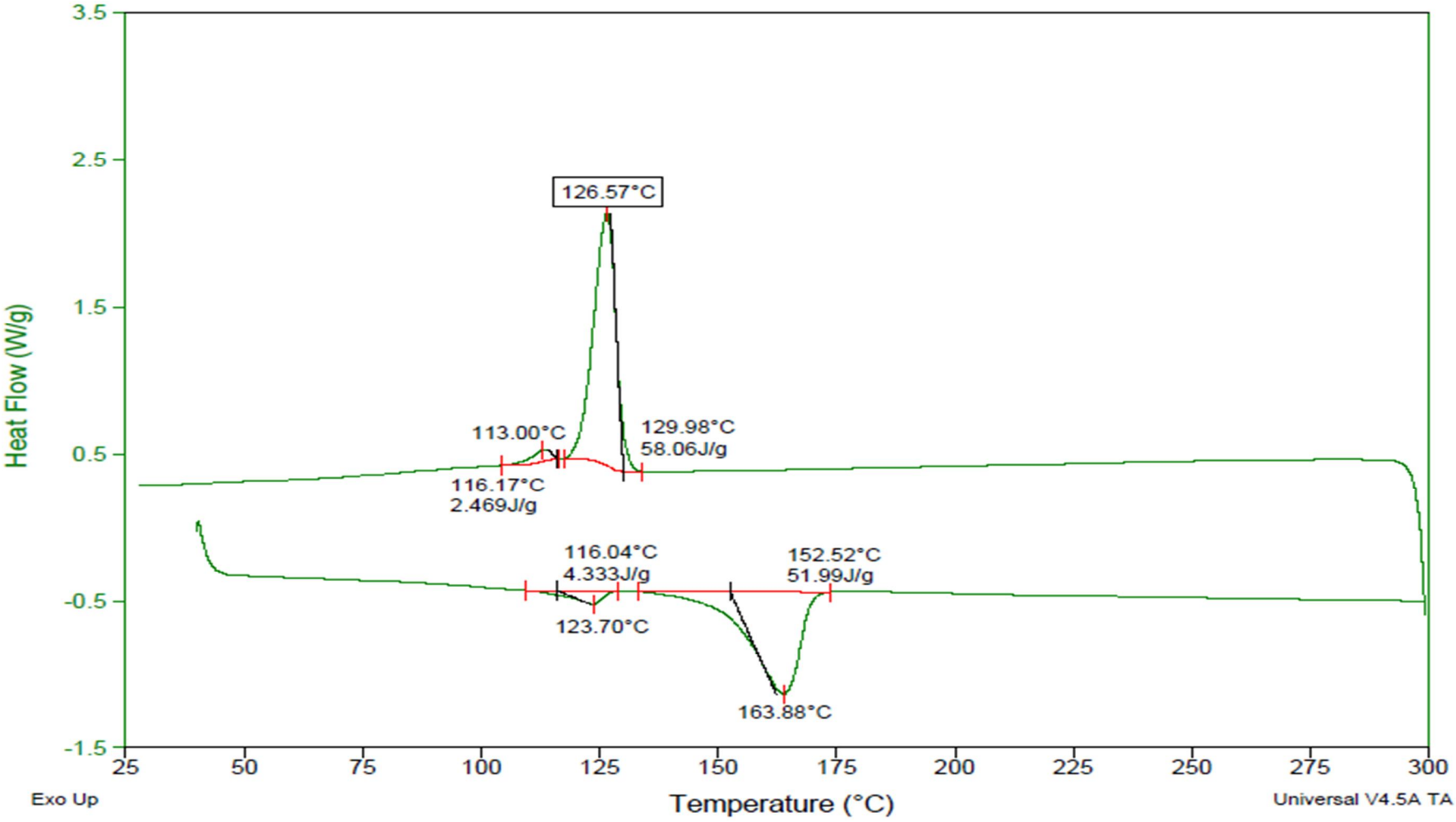

Figure A.2.24 : DSC diagram of RPP/10% EPDM/HPN 20E/I-168 ternary mixture

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